## CHARACTERIZATION OF ULTRAMAFIC MINE TAILINGS REACTIVITY FOR

## CARBON CAPTURE AND STORAGE

by

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#### Abstract

The carbon capture and storage potentials of ultramafic mine tailings are essential for assessing if mineral carbonation is a promising  $CO_2$  sequestration strategy.  $CO_2$  gas is mineralized in solid, stable carbonate minerals through dissolution and reaction with Mg-rich mining wastes. Here, the physical and chemical controls on reactivity and capacity for  $CO_2$  sequestration in systems representative of mine tailings are examined using a combination of experimental techniques including flow-through, batch dissolution and disk carbonation. The reactivity of tailings is measured as a number of  $Mg^{2+}$  that is loosely bounded and readily leached (termed labile Mg). The study deploys the definition of labile Mg and understands its variability for advancing carbon sequestration techniques on the pilot and field scale.

Flow-through and batch dissolution experiments on pure mineral phases and tailings show that labile Mg can be sourced from the bulk dissolution of Mg-hydroxides and the transient surface-reaction of Mg-silicates. Labile Mg is dependent primarily on mineralogy as well as the surrounding geochemical environment. CO<sub>2</sub> is the optimized acid that imposes a parallel and addictive effect towards promoting mineral dissolution and therefore enhances the quantity of labile Mg (reactivity). Characterizing mine tailings' reactivity based on the capacity of labile Mg extraction is fundamental for accurate estimation of the carbon sequestration potential of the deposits and decisions on employment of the proper carbon sequestration techniques. This research imparts methods for quantitatively determine the reactivity of carbon capture and storage using mine tailings. Aspects of this research, such as serpentine surface-exchange reaction, also enabled more in-depth observations into the dissolution pathways of Mg-silicates and the feasibility of using ultramafic mine tailings for long-term carbon capture and storage.

# Lay Summary

Increasing atmospheric  $CO_2$  concentration since the pre-industrial times as a result of anthropogenic input has led to enhanced global warming, climate change and ocean acidification. Storage of  $CO_2$  via mineral carbonation is a technology that has unlimited capacity to permanently store  $CO_2$  in an environmentally begin form via dissolution and carbonate mineral precipitation. Ultramafic mine tailings represent an attractive and cost-effective option to capture and store  $CO_2$ via mineral carbonation. This thesis contributes to developing tools and experimental approaches to define and estimate the  $CO_2$  sequestration potential (reactivity) of mineral phases and ultramafic mine tailings. We adopted and tested three different experimental set-ups for quickly and efficiently quantifying reactivity. We define reactivity as the proportion of the Mg cations that are labile, namely those that are loosely bounded, fast reacting, and readily leached at atmospheric conditions. Together, these results build a valuable foundation for the future advancement and implementation of carbon mineralization techniques at a larger scale.

#### Preface

This dissertation contains an introductory chapter, two research chapters (chapter 2 and chapter 3), and a conclusion chapter. The author and supervisor, Prof. Gregory Dipple, were responsible for project design and identification of research objectives. Prof. Dipple also provided guidance, advice and edits throughout the entire process of the research and in the writing of the dissertation. Prof. Ulrich Mayer and Prof. Roger Francois are credited for providing input at committee meetings and through independent correspondence. Dr. Jamie Cutts and Dr. Connor Turvey both gave invaluable pieces of advice and edits during the preparation of the dissertation. The author is responsible for the interpretation of data from each analysis under the supervision of Prof. Dipple. Specific contributions to each manuscript are described below.

A version of Chapter 2 has been prepared for submission to an international peer-reviewed academic journal. The manuscript is authored as follows: Lu, Dipple, Turvey, Cutts. Lu the author was responsible for sample preparation (crushing, sieving, mineral separation, mixing), and analytical work, characterizing each of the experimental samples as well as preparing all figures, data tables, and drafts of the manuscript submitted for peer review, publication and as a chapter for this dissertation. G.M. Dipple and the author conceived the study, designed the experiments. Turvey performed the hydrotalcite experiment, collected data as well as providing essential information on X-ray diffraction analysis (XRD) on clay minerals and hydrotalcite minerals. J.A. Cutts provided valuable expertise, advice, comments, careful reviews and edits throughout the complete process of the manuscript. The author wrote the manuscript with input from co-authors. All co-authors confirm that this is an accurate reflection of the author's contributions and agree to the use of this manuscript in this thesis. All sample preparation, chemistry, analytical work, and data reduction were carried out at UBC using facilities at the EOAS department except for whole-

rock geochemistry analysis (XRF), which were analyzed at ALS Minerals (ALS) in North Vancouver. The appendix to this chapter will be submitted as the supporting information to the manuscript.

Chapter 3 is written as a thesis chapter as part of the research chapters in this dissertation. The supervisor Prof Dipple and the author designed the experiments. The author conducted the experiments, Erin Gatdula and Mariana Garcia Iwasaki provided assistance in the laboratory with sampling. Frances Jones and Maureen Soon performed total inorganic carbon (TIC) analysis. Dr. Turvey contributed to the identification of the secondary dissolution product using XRD that significantly contribute to the conclusion of the data and experiments. The author interpreted the data with input from both Prof. Dipple and Dr. Turvey. The author is also prepared all the figures, data tables, drafting and writing of this chapter.

This research was presented at the 2nd De Beers Mineral Carbonation Workshop in 2018. The research was also presented at the AME Round-up conferences from January 2017 to January 2020, 2018 RFG (Resources for Future Generations) conference and the Goldschmidt Geochemistry Conference from 2019 to 2020.

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# List of Symbols

Mg<sup>2+</sup>–Mg cation

- [Mg<sup>2+</sup>] aqueous magnesium concentration
- $K^+$  potassium cation
- [K<sup>+</sup>] aqueous potassium concentration
- $\theta$  scattering angle of X-rays
- t-time
- $\Omega$  saturation index
- $R_{Mg}$  experimental dissolution rate based on [Mg] mol m<sup>-2</sup> s<sup>-1</sup>
- $r_f$  flow rate (L s<sup>-1</sup>),
- $\Delta_{[Mg]}$  difference between the effluent and the eluent [Mg] (mol L<sup>-1</sup>),
- $\eta_{Mg}$  mineral stoichiometric coefficient of Mg
- $m_0$  initial mass of mineral reactant (g)
- mol Mg m<sup>-2</sup> s<sup>-1</sup> –unit of reaction rate moles of Mg per m<sup>2</sup> mineral reactive area per seconds
- mol Mg g<sup>-1</sup> s<sup>-1</sup> –unit of reaction rate moles of Mg per g of sample per seconds
- %C % total inorganic carbon

# **List of Abbreviations**

- GHG Green house gas
- CCS Carbon capture and storage
- CCUS Carbon capture utilization and storage
- IPCC Intergovernmental Panel on Climate Change
- MKM Mount Keith Nickel Mine
- FT-TRA -Flow-through time-resolved analysis
- NaCl-sodium chloride
- CO<sub>2</sub> carbon dioxide gas
- Kr-krypton gas
- $pCO_2 CO_2$  partial pressure
- DIC dissolved inorganic carbon
- wt.% weight percent
- ml/min milliliter per min
- $\mu m micrometer$
- XRD X-ray diffraction
- TGA Thermogravimetric analysis
- $SEM-scanning\ electron\ microscopy$
- XRF X-ray fluorescence spectroscopy
- BET Brunauer–Emmett–Teller
- $A_{BET}$  (m<sup>2</sup> g<sup>-1</sup>) mineral reactive surface area
- Grain size d(0.9) um 90% mineral grain size in um
- [Mg]:[Si] aqueous concentration of Mg and Si ratio

- [Mg<sup>2+</sup>] aqueous Mg concentration
- [HCO<sub>3</sub><sup>-</sup>] aqueous bicarbonate concentration
- [H<sub>2</sub>PO<sub>4</sub><sup>-</sup>] aqueous bisphosphate concentration
- $\mathrm{H^{+}}-\mathrm{hydrogen}$  ion
- OH<sup>-</sup> hydroxide ion
- $\rm CO_3^{2-}-carbonate$  ion
- H<sub>3</sub>PO<sub>4</sub>- phosphoric acid
- MgHCO<sub>3</sub><sup>+</sup> magnesium hydroxyl-carbonates
- HCl- hydrochloric acid
- HNO<sub>3</sub> nitric acid
- H<sub>2</sub>CO<sub>3</sub> carbonic acid
- HPO<sub>4</sub><sup>2-</sup> hydrogen phosphate
- PO<sub>4</sub><sup>3-</sup> phosphate ion
- N<sub>2</sub> nitrogen gas
- ppm parts per million
- QAQC quality assurance and quality control
- brc brucite
- qtz quartz
- LM Lane Mountain
- ICP-OES inductively coupled plasma optical emission spectrometry
- TIC total inorganic carbon
- MgO-magnesium oxide
- pKa-acid dissociation constant

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I would like to dedicate this work to both of my dearest grandfathers Yanpeng Shi and Zhenzong Lu. I am sorry for not being able to say a final goodbye before I lose both of you forever. I love you both forever and always.

#### **Chapter 1: Introduction**

#### **1.1** Significance of the study

The global climate has been warming at a faster rate in the past 100 years than at any other time in the geological history; a trend largely attributed to the continuously increasing anthropogenic carbon dioxide (CO<sub>2</sub>) emissions since the industrial revolution (IPCC 2018). CO<sub>2</sub> provides the dominant means through which carbon is transferred in nature between several natural reservoirs, including the atmosphere, oceans, and the biosphere. The exchange between these reservoirs has been relatively consistent over geological time (Houghton 2005) until human activities beginning during the industrial revolution that significantly disturbed this balance. The burning of several hundred million tonnes of carbon for over 100 years is the leading cause of the current increasing CO<sub>2</sub> concentration in the atmosphere (Hellevang 2015; Oelkers et al., 2008; Songolzadeh et al., 2014). The apparent consequences of the rise in CO<sub>2</sub> level on human communities and ecosystems include global climate change, sea-level rise, reduced agriculture and food supply, ocean acidification, and loss of natural biodiversity (Houghton 2005). Therefore, the development of innovative carbon capture and storage technologies to mitigate the harmful effects of anthropogenic CO<sub>2</sub> emissions on the global climate system becomes increasingly important (Reay et al., 2007). The Inter-government Panel on Climate Change (IPCC) recently projects that a 45% reduction in greenhouse gas (GHGs) emissions will have to be achieved in the next 30 years to prevent >1.5 °C increase in global temperature by 2100 (Figure 1.1) (IPCC 2018).



Figure 1.1 Carbon dioxide emission pathways until 2100 and the extent of net negative emissions and bioenergy with carbon capture and storage (BECCS) in 2100, adapted from (Fuss et al., 2014).

Currently, a number of strategies and technologies are being studied and tested by many countries around the world to reduce anthropogenic CO<sub>2</sub> emissions (Keith et al., 2018; Markewitz et al., 2012). The proposed strategies include government policies such as the development of renewable energy, increasing energy efficiency and the implementation of carbon taxes. Other scientific approaches include the utilization of CO<sub>2</sub> for producing platform and bulk chemicals, the physical capture and storage of CO<sub>2</sub> for enhancing oil recovery (EOR), as well as the long term storage of CO<sub>2</sub> in geological rock formation (Bobicki et al., 2012; Hellevang 2015; Keith et al., 2018; Washbourne et al., 2012). Among these approaches, carbon mineralization, also known as mineral carbonation, is demonstrated to be: environmentally benign and stable, having high carbon storage capacity (G.T.), long storage time (millennia) and easy for post-storage monitoring (Lackner et al., 1995; Lackner et al., 1997; Seifritz 1990; Sipilä et al., 2008; Wadsworth 2003). Mineral

carbonation is a promising option that was first proposed by Seifritz (1990), and involves exploiting the natural mineral reactions that crystallize  $CO_{2(g)}$  from the atmosphere or fluid as a newly formed carbonate mineral.

In general, attempts to react  $CO_2$  with alkaline minerals have been implemented in two principal ways: (1) ex-situ carbon mineralization involves above-ground processes in which local capturing of atmospheric  $CO_2$  is accelerated by material comminution (Gerdemann et al., 2007); or (2) in-situ carbon mineralization, which involves the transport and direct injection of  $CO_2$  into existing rock formations (Power et al., 2013). In both cases, anthropogenic CO<sub>2</sub> is captured and stored through naturally reacting with alkaline earth metal bearing silicates and hydroxide minerals to form carbonate minerals. To date, potential feedstocks of carbon mineralization include but are not limited to subsurface mafic and ultramafic formations (Gislason et al., 2014; Hellevang 2015; Kelemen and Matter, 2008; McGrail et al., 2017; Oelkers et al., 2008; Paukert et al., 2012; Pogge von Strandmann et al., 2019; Power et al., 2013; Schaefer et al., 2011), chemical industrial waste stockpiles (Bobicki et al., 2012; Power et al., 2013) as well as pulverized rock or wastes from mining (Assima et al., 2013, 2014a; Pronost et al., 2011; Renforth et al., 2009; Phil Renforth et al., 2011; Renforth and Henderson 2017; Schuiling and Boer 2010; Washbourne et al., 2012; Wilson et al., 2009). Among these feedstocks, industrial wastes and mine wastes are most promising because mineral carbonation reactions occur at accelerated rates, owing to the reduced grain size of these materials compared to their natural counterparts. Examples of industrial wastes that have been exploited over the past decades as sinks for  $CO_2$  include steel and blast furnace slags, wastes from alumina production, and alkaline and saline wastewater, which all demonstrated inherently more reactive properties than natural minerals (Back et al., 2011; Bobicki et al., 2012; Dilmore et al., 2008; Eloneva et al., 2008; Ferrini et al., 2009; Huijgen and Comans 2006; Khaitan et al., 2010;

McCutcheon et al., 2019; Mignardi et al., 2011; Mills et al., 2010; Morales-Flórez et al., 2011; Power et al., 2014; Power et al., 2013; Pronost et al., 2011; Wilson et al., 2011; Wilson et al., 2006). In terms of mine wastes, those containing high Mg and Ca-silicate, -oxide, and -hydroxide minerals (Bobicki et al., 2012; Renforth et al., 2011) can sequester CO<sub>2</sub> through the liberation of Mg<sup>2+</sup> and Ca<sup>2+</sup> from mineral bulk dissolution and surface-ion exchange processes, followed by precipitation of carbonate minerals to permanently trap atmospheric CO<sub>2</sub> (Lackner 2003; Lackner et al., 1995; Lackner et al., 1997; Seifritz 1990). Many ultramafic mine sites around the world, such as the Mount Keith Nickel Mine in Western Australia and the Diavik Diamond Mine in the North West Territories, Canada, have documented their tailings naturally reacting with atmospheric  $CO_2$  at a rate of approximately 40,000 tonnes year<sup>-1</sup> and 400 tonnes year<sup>-1</sup>, respectively (Wilson et al., 2011, 2014). However, such natural carbonation processes are sluggish and inefficient due to the nature of chemical weathering at the earth's surface. (e.g. Harrison et al., 2013; Krevor and Lackner 2009; Power et al., 2013; Power et al., 2013). In order for mineral carbonation to be widely implemented as a climate change mitigation strategy, methods that can accelerate such chemical frameworks are needed. If accelerated mineral carbonation is integrated into mine site logistical planning, it could serve to reduce the CO<sub>2</sub> emissions at mine sites and bring the co-benefit of dust mitigation (Canadell and Raupach 2008; Huntzinger et al., 2009a, 2009b), tailings stabilization (Turvey et al., 2017; Vanderzee et al., 2019; Wilson et al., 2009) and toxic metal encapsulation (Hamilton et al., 2016, 2018).

Existing mineral carbonation acceleration technologies require significant input of energy (Bea et al., 2012; Oskierski et al., 2013; Pronost et al., 2011; Wilson et al., 2009, 2011; Wilson et al., 2006). Such strategies typically focus on industrial pre-treatment processes that use high-temperature and pressures (e.g., 185°C, 150 atm), elevated CO<sub>2</sub> concentrations, and high-energy

attrition to accelerate mineral reaction kinetics and increase CO<sub>2</sub> storage capacity (Béarat et al., 2004; Fagerlund et al., 2012; Gerdemann et al., 2007; Koukouzas et al., 2009; Krevor and Lackner 2011; Li et al., 2018a; Sanna et al., 2014; Sipilä et al., 2008). Nevertheless, consumption of resources and financial cost make these techniques work-intensive and, thus, not very carbonefficient. The greatest cost-benefits and, thus, the most attractive option financially, is to promote mineral dissolution and carbonation at atmospheric temperature and pressure; however, the variables affecting the behavior of the reactions at such conditions have not yet been studied extensively. One of the primary factors controlling the capacity of mineral carbonation at a mine site is the tailings' reactivity, which can be controlled by mineral composition, chemical environment, as well as the mineral processing procedure (Li et al., 2018b; Lindsay et al., 2015; Oskierski et al., 2013; Santos et al., 2015; Uddin et al., 2012; Wilson et al., 2014). To better predict the fate of CO<sub>2</sub> in tailings storage facilities and to correctly estimate the CO<sub>2</sub> sequestration capacity, the understanding of controls on tailings' reactivity for carbon sequestration needs to be further investigated and comprehended. Specifically, effects from the geochemical environment and mineralogy must be considered.

In this study, we carried out three types of bench-scale laboratory tests on ultramafic minerals and tailings to provide insight into our current understanding of mineral dissolution mechanisms under ambient conditions and how they control the quantifications of tailings' reactivity for carbon sequestration. These experimental investigations are designed with a common objective to test the variability of tailings' reactivity efficiently and economically. The scope of the experiments spanned from the batch and flow-through dissolution to coupled dissolutionprecipitation reaction, which together provides vital understandings of the effect from water saturation, solution chemistry, mineral reactive surface area, mineral abundance, and reaction

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kinetics on tailings' reactivity for carbon sequestration. The experimental results are presented in the context of their application to accessing  $CO_2$  sequestration potential in ultramafic mine tailings and with the broader implications of constructing testing protocols for evaluating the carbon sequestration reactivity of ultramafic mine sites around the world.

The following sections present a comprehensive overview of ultramafic rocks and related minerals, different types of hydrated magnesium carbonates found in ultramafic tailings, a summary of the significance of defining tailings' reactivity using mineral dissolution kinetics, as well as the related geochemical concepts. The background information is followed by an overview of the dissertation and an abstract of each research chapter.

## **1.2** Ultramafic minerals and tailings

Ultramafic rocks are rocks typical of the mantle and occur in such geological settings as the base of ophiolites, one of the components of intrusive complexes, and in kimberlite pipes. The most common ultramafic rock is peridotite (40-98% olivine), which comprises most of the earth's upper mantle and is exposed along plate boundaries by tectonic uplift. Primary mafic (ferromagnesium) minerals typical in ultramafic rocks are olivine, pyroxene, hornblende, mica, as well as aluminum-bearing minerals (e.g. plagioclase, spinel, garnet). Alteration minerals include serpentine, chlorite, magnetite, and brucite, of which serpentine minerals are the most abundant. These alteration minerals are commonly formed through serpentinization, a metamorphic transformation that involves the hydration of olivine and orthopyroxene (Moody 1976; Power et al., 2013). The main serpentinization hydration reaction of the olivine Mg-end-member forsterite will yield serpentine and brucite, which represents the most common Mg-silicate and -hydroxide phases in serpentinites (Eq.1).

$$2Mg_2SiO_4 + 3 H_2O \rightarrow Mg_3Si_2O_5(OH)_4 + Mg(OH)_2$$
 Eq. 1

#### Forsterite Serpentine Brucite

Serpentine is a mineral group that comprises antigorite  $[(Mg,Fe)_3Si_2O_5(OH)_4]$ , lizardite  $[Mg_3Si_2O_5(OH)_4]$  and chrysotile  $[Mg_3Si_2O_5(OH)_4]$ . Brucite, on the other hand, often represents the minority in ultramafic rocks and can be quickly carbonated to form hydrotalcite at the earth's surface condition. Brucite and hydrotalcite are both hydroxide phases that are highly reactive and, thus, can sequester  $CO_2$  quickly. Brucite is a hydroxide magnesium octahedra, while hydrotalcite is layered double hydroxide (LDH) minerals that consist of brucite-like layers. Hydrotalcites are composed of divalent and trivalent cations, interlaying weakly bounded H<sub>2</sub>O molecules and anions such as  $SO_4^{2-}$ ,  $NO_3^{-}$  and  $CO_3^{2-}$  (Mills et al., 2012). In general, hydrotalcite can form through metamorphic

processes operating at high temperatures mainly through the hydrothermal alteration of spinel minerals (e.g. Ashwal and Cairneross 1997; Grguric 2003; Grguric et al., 2001; Melchiorre et al. 2017, 2018) or through low-temperature carbonation of Fe-brucite. High-temperature hydrotalcite can sequester CO<sub>2</sub> through anion exchange processes, while hydrotalcite of low-temperature from Fe-brucite is already a carbonation product (Turvey et al., 2018). Overall, the abundance of serpentine in ultramafic rocks is much higher than that of brucite or hydrotalcite (Moody 1976), which makes them the major contributor for mineral carbonation in ultramafic mine tailings.

Ultramafic rocks are of economic interest due to their association with mineral resources such as chromite, corundum, nickel, olivine and platinum-group elements (PGE's). The primary minerals chromite and olivine are the typical hosts for PGE mineralization, whereas corundum and nickel are often related to secondary processes, either through metamorphism or chemical weathering (Lesure et al., 1993). During the ore extraction process, serpentine and brucite are usually separated from the valuable economic fraction of the ore and are disposed of as waste materials (tailings) that enable the subsequent carbonation process.

Common Mg-carbonates formed through the carbonation of ultramafic minerals include lansfordite [MgCO<sub>3</sub>·5H<sub>2</sub>O], nesquehonite [MgCO<sub>3</sub>·3H<sub>2</sub>O], dypingite [Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·5H<sub>2</sub>O] and hydromagnesite [Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O] (Bea et al., 2012; Beinlich and Austrheim 2012; Wilson et al., 2009; Wilson et al., 2006) (Figure 1.2). These are carbonate minerals with a high content of magnesium and can be organized into three groups based on their chemical formula. The first group consists of minerals with formulas based on magnesite (MgCO<sub>3</sub>) with variable degrees of hydration. Examples of such minerals include nesquehonite (Giesting et al., 2012) and lansfordite (Hill et al., 1982). The second group of hydrated magnesium carbonate has an additional hydroxyl group (or brucite-like component) compared to the first group. Artinite (Akao and Iwai 1977a) and pokrovskite (Perchiazzi and Merlino 2006) are both members of this group. Finally, the third group includes minerals with the chemical formula of  $[Mg_5(CO_3)_4(OH)_2 \cdot xH_2O]$ . Three minerals include hydromagnesite (Akao and Iwai 1977b; Akao et al., 1974), dypingite and giorgiosite are members of the third group with different water content. They are also typical carbonate phases found in carbonated ultramafic tailings (Wilson et al., 2009).



Figure 1.2 SEM (Scanning electron microscope image) of common hydrated Mg-carbonate phases found in tailings formed through mineral carbonation (Power et al., 2013). Hydromagnesite SEM image, adapted from (Power et al., 2009).

## **1.3** Control on the dissolution kinetics

### **1.3.1** Mineral structure of ultramafic minerals

The dissolution and precipitation rate of minerals are often associated with their euhedral crystal surfaces (Aspandiar and Eggleton 2006; Eggleston and Hochella 1992; Maurice et al., 1995). Previous SEM studies demonstrate that mineral crystallography controls their dissolution kinetics, especially for minerals with relatively flat crystal faces (Brantley and Chen 1995, 2018; Schott and Berner 1983; White and Brantley 1995). Among the group of ultramafic minerals, olivine (forsterite-Mg endmember: Mg<sub>2</sub>SiO<sub>4</sub>) and serpentine are representative silicate minerals that have large surfaces for dissolution. In particular, serpentine is a phyllosilicate (sheet silicate) with a nominal composition of  $[Mg_3Si_2O_5(OH)_4]$  and consists of alternating tetrahedral Si layers and octahedral (brucite-like) Mg layers. The tetrahedral sheets of serpentine are connected to the octahedral sheets through the nonshared apical oxygen of the tetrahedra, and they are 1:1 layered structure (Bales and Morgan 1985; Daval et al., 2013; Pokrovsky and Schott 2000; Power et al., 2013; Pronost et al., 2011). As shown in Figure 1.3, the layers within the serpentine mineral crystal structure are linked by hydrogen bonds that are long and weak. The variable arranged Si and Mg layers give rise to complex polymorphs of serpentine include flat-layer lizardite, tubular chrysotile and wave-like antigorite (Lacinska et al., 2016; Calle and H 1988). In contrast, olivine (Mgendmember forsterite) is a nesosilicate with a structure that consists of individual silicon-oxygen tetrahedra linked by magnesium atoms. As such, its dissolution mechanism is less complex than most other naturally occurring multi-oxide silicates (Oelkers et al., 2001a).



Figure 1.3 Schematic representation of serpentine minerals crystal structure, including A) flat layer lizardite,B) tubular chrysotile, C) modulated antigorite (Mevel, 2003), adapted from (Lacinska et al. 2016).

For most minerals, the underlying control of the dissolution characteristics is a function of the mineral's crystal structure and the destruction of the slowest-breaking bond essential to the crystal structure (typically, the shortest and strongest bond) (Schott et al., 2009). Dissolution of single oxide minerals such as brucite, breakage of only one type of bond is required, whereas, for multi-oxide minerals such as olivine and serpentine, numerous metal-oxygen bonds need to be broken (Figure 1.4) (Béarat et al., 2004; Jarvis et al., 2009; Luce et al., 1972; Pokrovsky and Schott 2000a; Schott et al., 2009). The dissolution and growth of serpentine often occur at specific sites on two types of surfaces, the basal surface parallel to the layers and the edge surface (Figure 1.4). Each surface has its distinct electrical charge, metal-oxygen bond characteristics, and the degree of hydroxylation in aqueous solutions (White and Brantley 1995). The relative difference in Si-O and metal-O bond strength may lead to non-stoichiometric or incongruent dissolution and the

preferential release of metal cations; which is typical of the initial surface ion-exchange reaction of serpentine dissolution (Béarat et al., 2004; Jarvis et al., 2009; Luce et al., 1972; Pokrovsky and Schott 2000a; Schott et al., 2012; Schott et al., 2009). As for the dissolution behavior of olivine, the dissolution can proceed by the breaking of just the ionic Mg-O bonds, liberating SiO<sub>4</sub><sup>4-</sup> anions directly into the solution. Due to both the absence of covalent Si-O-Si bonds and the relative weakness of the metal-oxygen bonds in its structure, olivine is among the fastest dissolving silicate minerals (e.g. Oelkers et al., 2018).



Figure 1.4 Schematic diagram showing brucite bulk dissolution versus serpentine surface-reaction. Serpentine crystal structure composes of 1:1 layer of brucite and tetrahedra silicate.

## **1.3.2** Other controls on dissolution

Aside from crystal structures, surface chemical properties also exert primary control on reaction rates of minerals in aqueous solutions. When mineral surfaces become hydrated in acidic solutions, protons  $(H^+)$  and hydroxyl ions  $(OH^-)$  will be adsorbed to the surface. The number of reactive sites on the mineral surfaces depends on the surface density and protonated sites (a function of pH). Both brucite and serpentine have shown faster dissolution rates in solutions with a high concentration of H<sup>+</sup> (lower pH) (Daval et al., 2013; Mellini 1982; Pokrovsky and Schott 2004) suggesting that, under acidic condition, lower pH will assist the extraction of Mg<sup>2+</sup> for carbon mineralization. In solutions with the presence of inorganic or organic ions and molecules (known as ligands), dissolution is more complicated since such molecules will also adsorb to the mineral surface and extract the attached metal cations (e.g. Mg<sup>2+</sup>). Ligands (e.g., oxalate, citrate, bicarbonate) can significantly enhance or inhibit mineral dissolution rates. The ligand effect on mineral carbonation arises due to the formation of carbonate ligands from the uptake of CO<sub>2</sub> into solution; the infiltration of CO<sub>2</sub> into solution is generally expected to accelerate mineral dissolution through the decline in pH as a result of the formation of carbonic acid (H<sub>2</sub>CO<sub>3</sub>), and bicarbonate ligand (HCO<sub>3</sub><sup>-</sup>).

Many integrated mineral carbonation processes proposed for carbonation of ultramafic mine wastes use thermal activation as a pre-treatment process. Silicate mineral dissolution rates are typically accelerated with increasing temperature, beginning at 220-180°C (Li et al., 2018b). However, heat pre-treatment will generate high energy consumption and is not economically viable for most mine sites. Mineral dissolution rate at atmospheric temperature and pressure is, therefore, a more economically promising strategy. Ultramafic tailings, which are generated through the milling of the valuable ore rocks, commonly have high reactive surface areas due to their high serpentine content and the ore crushing process (Wilson et al., 2009, 2011). Mg-bearing silicates and hydroxide minerals with higher accessible reactive surface areas often contribute to enhanced dissolution reaction, which makes tailings storage facilities of ultramafic-hosted mine sites an ideal location for mineral carbonation. Introducing agitation methods such as stirring and shaking, will typically promote liquid recirculation, which could potentially increase the reactive surface area on the micro-scale and, thus, enhance mineral dissolution rate (Harrison et al., 2017; Khaitan et al., 2010; Li et al., 2018b; Metz and Ganor 2001).

### 1.4 Labile Mg and reactivity

Accurate estimation of tailings' reactivity for carbon sequestration would enable mine sites to make better decisions in terms of the implementation of their carbon capture and storage techniques. In order to maximize the economic feasibility of mineral carbonation techniques at mine sites, process routes involving low-temperature and pressure should be considered to achieve carbon mineralization at mine scales and rates sufficient to help offset mine emissions. Specifically, the CO<sub>2</sub> sequestration potential of tailings is strongly dependent on the proportion of the metal cations that are readily released during mineral dissolution. Cations that are loosely bound, fast reacting, and readily leached under atmospheric conditions are ideal, referred to herein as 'labile' cations. Because Mg<sup>2+</sup> is the most abundant metal cations in ultramafic rocks, labile Mg<sup>2+</sup> thus becomes the target for mineral dissolution and the precipitation of Mg-carbonates. The labile portion of Mg<sup>2+</sup> from Mg-silicates is still uncertain, and the labile characteristic of polymetallic tailings' materials is still yet to be determined. Depending on the carbon sequestration approach, factors including mineral content and the geochemical conditions will dictate the release rate and content of labile Mg in individual samples and deposits. Given the relatively sluggish kinetics of dissolution under ambient condition and the mild acidity present in many tailings' facilities, targeting the labile Mg present in the minor but highly reactive phases such as brucite should probably be prioritized over the long-term bulk dissolution of relatively unreactive silicate phases. Establishing a more comprehensive understanding of tailings' reactivity for mineral carbonation using the concept of labile Mg is the theme of this thesis and the rationale behind the design of the three sets of laboratory experiments.

### **1.5** Experimental approaches

Three types of experiments are used to access mineral and tailings' reactivity for mineral carbonation, including batch, flow-through dissolution and disk carbonation. Flow-through dissolution is commonly used to investigate dissolution behavior under conditions of fixed solution chemistry. Posey-Dowty et al. (1986) provide an overview of experimental approaches using flowthrough reactors, of which continuously-stirred tank reactors (CSTR; Rimstidt and Dove, 1986), fluidized-bed reactors (Chou and Wollast 1985) and plug-flow reactors (Johnson et al., 1998) are the most commonly used types. In this study, the applicability of "flow-through time-resolved analysis" (FT-TRA) to measure the rate and content of labile Mg in different minerals and tailings is investigated (De Baere et al., 2015). In the FT-TRA flow-through system, the amount of solids subject to dissolution and the volume is much smaller than the conventional flow-through reactor. Because of the small volume, much shorter inlet solution residence times can be achieved in the reactor, which reduces the time needed to reach the steady-state of dissolution. Fluid flows in FT-TRA at a constant rate and is sampled at the exits point. The continuous flow of fluid through the reactor ensures that the experiments remain undersaturated with respect to secondary phases and allows for systematic manipulation of input solute concentrations. The dissolution rate is proportional to the difference in the outlet and inlet concentration of Mg released from the sample by dissolution. Magnesium concentration of the exit fluid is considered representative of that inside the reactor and is used for quantifying labile Mg content.

Batch experiments at specific  $CO_2$  pressure and acid concentration are carried out in closed vessels for similar dissolution studies of minerals and tailings. Earlier mineral dissolution studies that involve batch reactors include Grandstaff (1997), Rimstidt and Barnes (1980), Schott et al. (1981) and Hövelmann et al.(2012a) during which a fixed amount of solids react with aqueous solutions in a closed-system container (Grandstaff 1977; Rimstidt and Barnes 1980; Schott et al., 1981). Solution compositions are sampled periodically since materials dissolution can lead to fluctuations in pH, ionic strength and elemental concentration. In this thesis, batch dissolution experiments are performed on a subset of samples used for the flow-through because it is investigated as an alternative option for quantifying labile Mg content of minerals and tailings. The dissolution rate can be expressed as the release rate of Mg and is compared with that measured using the flow-through. Both batch and flow-through dissolution are used to investigate reactivity through monitoring the dissolution behavior of minerals and tailings. Based on experimental results from both dissolution studies, labile Mg content is defined based on the rate and fraction of Mg<sup>2+</sup> reacted of the tested minerals and tailings.

A third experimental approach developed in this thesis is the disk carbonation experiment. This experiment simulates aqueous carbonated solution percolation through solids that simulate the mineral carbonation reactions in real tailings' storage environment. Disk carbonation is inspired by the conventional column experiments and is designed to investigate the controls on mineral carbonation in partially saturated pores supplied with  $CO_{2(g)}$ . The experiment involves a coupled mineral dissolution-precipitation reaction, and reactivity is characterized by converting labile Mg content to solid Mg-carbonate minerals. This approach directly measures the evolution of mineral dissolution and Mg-carbonate precipitation reaction progress. Experiments of this type do not readily yield fundamental kinetics data, but they do provide a new pathway for evaluating reactivity.

### **1.6** Objectives and organization

The objective of this thesis is to characterize and assess the CO<sub>2</sub> sequestration potential of ultramafic minerals and tailings. A combination of experimental, analytical and modelling techniques are used to define the concept of labile cations based on mineral dissolution rate and fraction of the sample reacted. We expect that labile cations content will depend on mineral compositions and geochemical environment (i.e. acid types and pH). Geochemical modelling is used to understand solution chemistry for better data interpretation. Major components of the study include labile Mg content characterization using flow-through dissolution and comparison of that with results obtained by performing batch dissolution and disk carbonation experiment using the same set of solid samples.

Two chapters are assembled to describe these investigations. The second chapter of this thesis (chapter 2) presents the first experimental protocol for testing reactivity using a flow-through reactor (FT-TRA). The chapter addresses how mineral dissolution rates of different minerals and tailings vary as a function of mineral structure, dissolution mechanism, and acid strength. Two complex tailings samples are included to translate mineralogical dissolution behavior to the reactivity of tailings for future application of carbon sequestration techniques. Chapter 3 builds on chapter 2 by adopting additional approaches. Batch dissolution and disk carbonation experiments are employed on a subset of samples used in chapter 2 to validate the results presented in chapter 2. Batch dissolution and disk carbonation experiments are designed to develop faster and less labour and economic intensive methods for measuring tailings' reactivity. The experimental results from the batch dissolution and disk carbonation are compared with results from chapter 2 and are discussed in the context of replacing flow-through as new experimental techniques for characterizing tailings' mineral carbonation reactivity. The results offer insights for both reactions

processes at the mineral interface and the pore scale. Finally, chapter 4 synthesizes the results of chapters 2 and 3 to give insights on labile Mg variability and the development of testing protocols to assess tailings reactivity better. The advantages and disadvantages of each experimental protocol are discussed and concluded. The chapter evaluates the three experiments, respectively and provides innovative ideas for new areas of research and experimental designs.

# Chapter 2: Characterizing labile Mg using flow-through dissolution

## 2.1 Introduction

As carbon dioxide concentrations in the atmosphere continue to rise, contributing to anthropogenic climate change (IPCC, 2017), there is an increased necessity and demand for developing carbon capture, utilization, and storage technologies (CCUS). The Inter-Government Panel on Climate Change (IPCC) has recently declared that global warming of the Earth's atmosphere should be limited to below 1.5 °C by 2100 to help mediate adverse impacts upon the environment and the society (IPCC, 2018b). One of the significant challenges in achieving this goal is that global greenhouse gas (GHG) emissions will have to be reduced by 45% before the year 2050 (IPCC, 2018b). Many strategies have been proposed and are undergoing research and development to capture, store, or utilize the excess carbon dioxide (CO<sub>2</sub>) (Broecker, 2007; Hoffert et al., 2002; Pacala and Socolow, 2018).

One such proposal is carbon mineralization, also known as mineral carbonation (Lackner et al., 1995; Seifritz, 1990). Carbon mineralization traps and stores  $CO_2$  via the formation of solid carbonate-bearing minerals, mitigating  $CO_2$  accumulation in the atmosphere. These reactions require sources of  $CO_2$  (often in the form of  $HCO_3^-$  and  $CO_3^{2-}$  anions) and divalent metal cations (such as  $Mg^{2+}$ ,  $Ca^{2+}$  and  $Fe^{2+}$ ). Carbonate anions may then react with alkaline earth cations to precipitate carbonate minerals (Eqn. 1-5). Wilson et al., (2010) found that upon precipitation of Mg-carbonate such as dypingite [Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·5H<sub>2</sub>O], the rate of mineral precipitation often outpaced the rate of  $CO_2$  dissolution and hydration in solution, which suggest that  $CO_2$  uptake may be rate-limiting (Power et al., 2013).

$$CO_{2(g)} \leftrightarrow CO_{2(aq)}$$
 (1)  
 $CO_{2(aq)} + H_2O_{(l)} \leftrightarrow H_2CO_{3(aq)}$  (2)  
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$$H_{2}CO_{3(aq)} \leftrightarrow HCO_{3}^{-}{}_{(aq)} + H^{+}{}_{(aq)} (3)$$
$$HCO_{3}^{-}{}_{(aq)} \leftrightarrow CO_{3}^{2}^{-}{}_{(aq)} + H^{+}{}_{(aq)} (4)$$
$$M^{2+}{}_{(aq)} + CO_{3}^{2-}{}_{(aq)} \leftrightarrow MCO_{3(s)} (5)$$

Moreover, waste from steel slags, fly ash, and naturally occurring mafic and ultramafic rocks are ideal feedstocks of divalent metal cations (Power et al., 2013; Romanov et al., 2015). For mafic and ultramafic rocks, mineral carbonation is a naturally occurring weathering process that is part of the global carbon cycle (Lackner et al., 1995; Moody, 1976; Oelkers and Cole, 2008). It has been estimated that carbon mineralization of mafic and ultramafic rocks has the capacity to sequester more than 10<sup>5</sup> Gt of CO<sub>2</sub> (Lackner, 2003); which is much larger than the annual global anthropogenic emission (i.e. ~33 Gt in 2019) (IPCC, 2007), however, these natural weathering processes are not fast enough to offset anthropogenic CO<sub>2</sub> emissions. Numerous process routes involving both high and low-temperature chemical reactions have been proposed in the literature to achieve carbon mineralization at a scale and rate sufficient to help mitigate global climate change. The geochemical processes fundamental to carbon mineralization are (1)  $CO_2$  dissolution generates acidic conditions, (2) mineral dissolution releases cations, consumes acidity and produces alkaline pH that allows (3) carbonate mineral precipitation that sequesters  $CO_2$ . These processes operate naturally under atmospheric conditions but may be manipulated in engineered systems that are designed to sequester CO<sub>2</sub> at faster rates (Power et al., 2013).

Industrial processes, such as the milling that occurs during mining of mafic and ultramafic rocks, drastically increase the reactive surface area of the rocks by the reduction in grain size. The carbonation processes, thus, are accelerated to the point where they have the potential to offset significant emissions within the next 30-80 years, the timescale required to keep global warming to 1.5 °C by 2100 (IPCC, 2018a). These accelerated weathering processes have been observed in

ultramafic mine wastes at many mine sites across the globe. For example, at the Mount Keith Nickel mine in Western Australia, Australia and the Diavik Diamond Mine in the Northwest Territories, Canada, atmospheric CO<sub>2</sub> is sequestered at rates of 40,000 tonnes year<sup>-1</sup> and 400 tonnes year<sup>-1</sup>, respectively (Wilson et al., 2011, 2014). These rate of carbonation could represent a significant offset of the mine sites CO<sub>2</sub> emissions and help with dust mitigation (Canadell and Raupach, 2008; Huntzinger et al., 2009b, 2009a), tailings stabilization (Turvey et al., 2017; Vanderzee et al., 2019; Wilson et al., 2009) and toxic metal encapsulation (Hamilton et al., 2018, 2016).

Various strategies are being developed to increase the reaction rate and carbon sequestration capacity of mafic and ultramafic mine wastes even further. Many engineering strategies for improving the efficiency of ultramafic tailings carbonation include the use of elevated temperatures and pressures (e.g., 185°C, 150 atm) to accelerate the mineral dissolution and carbonation processes (Béarat et al., 2004; Fagerlund et al., 2012; Gerdemann et al., 2007; Koukouzas et al., 2009; Krevor et al., 2011; Li et al., 2018; Sipilä et al., 2008; Zevenhoven et al., 2008). While they are effectively increasing reaction rates, such methods are typically associated with substantial energy consumption and financial costs and, thus, they may be more work-intensive and less carbon-friendly. These drawbacks can potentially be avoided by improving the efficiency of the mineral dissolution and carbonation reactions under atmospheric conditions, and by characterizing reactivity of materials and thereby maximizing the economic feasibility of mineral carbonation at mine sites.

The rate of carbon sequestration in mine wastes at atmospheric conditions is dependent on two major parameters, the dissolution rate of existing ultramafic minerals that act as the feedstock of divalent cations, and the precipitation rate of the newly forming carbonate minerals. However, when considering the first parameter, the reactivity of a tailings pile varies substantially due to

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heterogeneity in mineral composition throughout an ultramafic deposit and the chemical composition of those different minerals. In many ultramafic deposits,  $Mg^{2+}$  is the most prevalent divalent cation available for reaction, which makes them the primary target for mineral carbonation (Hamilton et al., 2018; Huijgen and Comans, 2006; Romanov et al., 2015). Various ultramafic minerals contain different proportions of  $Mg^{2+}$  within their crystal structures, and the shape of their crystal structure often dictates the rate at which the  $Mg^{2+}$  becomes available for carbonation reactions. Cations that are loosely bound and become rapidly available can be referred to as "labile" (Aoba et al., 1992; Daval et al., 2013; Tosca and Wright, 2018). The presence or absence of labile cations in the various minerals found within ultramafic tailings will thus, determine the capacity for carbon sequestration. Labile cations also suggest that estimating the presence of different Mg-minerals and characterizing their dissolution behavior is essential for attempting to predict carbon sequestration potential.

In ultramafic rocks, labile cations are often sourced from minerals such as serpentine [Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>] and brucite [Mg(OH)<sub>2</sub>]; however, even these two sources of labile cations have very different dissolution behaviors (Bach et al., 2006; Moody, 1976; Schrenk et al., 2013). Mg-hydroxide minerals, such as brucite, can undergo full dissolution within a short period (Béarat et al., 2004; Jordan and Rammensee, 1996; Pokrovsky et al., 2005; Vermilyea, 1969). In contrast, the dissolution of sheet Mg-silicates, such as serpentine is much slower and remains rather challenging to understand without fully modelling the kinetic reaction paths (Daval et al., 2013; Krevor and Lackner, 2011; Martinez et al., 2014; Palandri and Kharaka, 2004). Furthermore, the dissolution behavior of different minerals will change depending on the geochemical environment (acid type, pH and the presence of ligands). Many published studies emphasize on investigating the dissolution kinetics of minerals over a wide range of conditions, to understand their weathering behaviors in

the natural environment (Amram and Ganor, 2005; Daval et al., 2013; Harrison et al., 2013a; Jordan and Rammensee, 1996; Lechat et al., 2016; Mellini, 1982; Metz and Ganor, 2001; Pokrovsky and Schott, 2004; Pokrovsky et al., 2005; Rozalen and Huertas, 2013; Stumm, 1997; Thom et al., 2013; Vermilyea, 1969). However, none of them can be used to accurately predict the dissolution rate at conditions relevant to  $CO_2$  sequestration (e.g. temperature 25°C and 0.0004 bar p $CO_2$ ). In particular, no study has addressed the use of  $CO_2$  to accelerate the transient and early-stage dissolution rate of serpentine and to extract "labile Mg" for mineral carbonation. While some studies have suggested that the presence of  $CO_2$  will affect the dissolution rate of silicate minerals through acidity and proton activated dissolution (Carroll and Knauss, 2005; Golubev et al., 2005; Prigiobbe et al., 2009), others have reported higher dissolution rate at high p $CO_2$ , possibly due to the rate-promoting effect of dissolved carbonate species (Berg and Banwart, 2000).

In this chapter, we aim to investigate mineral dissolution kinetics as a means of assessing the reactivity of minerals and ultramafic mine tailings under conditions that prevail for mineral carbonation. Flow-through dissolution experiments were performed on Mg-hydroxide and silicate minerals, together with tailings that are typical within ultramafic deposits. The study intended to, 1) propose the concept of labile Mg based on its release rate from minerals being above a selected value, and the fraction of Mg<sup>2+</sup> reacted from minerals and tailings at a rate above the chosen value, 2) examine the variability of labile Mg as a function of acid types, acid strength and mineralogy, 3) discuss the implications of labile Mg for implementing real-world carbon sequestration technology at mine sites.

## 2.2 Materials and methods

### 2.2.1 Materials

Samples of natural serpentine, natural brucite, synthetic hydrotalcite and two ultramafic tailings were acquired for this study. Because brucite is found at variable weight percent in ultramafic tailings to a maximum of 12% (Harrison et al., 2013b), a proxy brucite sample was created for these experiments by mechanically mixing 10 wt% high-purity brucite ore with 90 wt% quartz sand. The brucite ore (sourced from Brucite Mine, Nevada) and quartz sand (product of Lane Mountain Materials) were pulverized using a ring mill and sieved to a grain size of 53-106  $\mu$ m at the University of British Columbia prior to mixing and characterization. The natural serpentinite sample was obtained from the Swift Creek landslide in northwest Washington, U.S.A. (Bayer and Linneman, 2011), in August 2014. The sample was ground using a jaw crusher and pulverized in a ring mill for two minutes before being dry sieved to a diameter of 53-106 µm. Crushed rock samples were obtained and represent likely tailings for two deposits. The rocks were sourced from the FPX Nickel Property in central British Columbia, Canada and the Gaucho Kué Mine in Northwest Territories, Canada. The nickel sample (BD-FPCOM) was collected from a metallurgical test that involved processing potential ore and extracting nickel. The diamond (GK-PK21) sample is representative of processed kimberlite from the Gaucho Kué Mine. Both samples were pulverized and dry sieved to the same grain size (53-106 µm) as the brucite and the serpentine. Samples of pure minerals were ultrasonically cleaned using pure ethanol to remove fine particles before rinsing with ultra-pure water (resistivity  $\geq 18.2 \text{ M}\Omega$  cm) for 5 minutes and air-dried at room temperature. The tailings samples were subjected to an additional "wet-sieving" treatment (sieving while suspended in deionized water) to further remove fine particles before undergoing similar processing to the mineral samples.

Before the dissolution experiments, the samples were characterized for their quantitative mineralogy, Brunauer-Emmett-Teller (BET) surface area (Fagerlund, 1973; Naderi, 2015; Sing, 2001), and particle size distributions, which are reported in Table 2.1. Qualitative and quantitative powder X-ray diffraction (XRD) was performed to quantify mineral abundances and test for homogeneity in all the starting materials. Prior to analysis, the samples were grounded under anhydrous ethanol in a McCrone® micronizing mill and dried overnight at room temperature. Backloading cavity powder mounts were prepared against coarse sandpaper. This procedure is performed to minimize the preferred crystallographic orientation. Measurements were collected using a Bruker D8 Focus Bragg-Brentano diffractometer with a LynxEye detector. A long, fine focus cobalt X-ray tube was operated with CoK- $\alpha$  radiation at 35 kV and 40 mA. Data were collected with a 0.03° 20 step size and a counting time of 7 s/step over a range of 3-80° 20. Search/match qualitative phase identification was completed with DIFFRACplus Eva 14 software (Bruker AXS, 2008) using the International Centre for Diffraction Data PDF-4+ 2010 database. Topaz Version 5 software (Bruker AXS) was used for quantitative Rietveld refinement of identified phases (Bish and Howard, 1988; Wilson et al., 2009a). It should be noted that clay minerals, such as serpentine, smectites are typically challenging to identify using X-ray diffraction due to the layered nature of their mineral structure (Turvey et al., 2017, 2018a, 2018b). For minerals present in low abundances, the absolute abundances are somewhat uncertain due to the nature of quantitative XRD analyses (Turvey et al., 2018a) and relative errors tending to increase for phases present at <2 wt% abundance (Dipple et al., 2002, Raudsepp et al., 1999; Turvey et al., 2017; Wilson et al., 2009c, 2006). Brucite is particularly prone to be incorrectly estimated, with relative errors as high as 250 % (Turvey et al., 2018a); when brucite is present at 0.2-2 wt%, 10% and >50%, the relative errors are typical ~90 %, 25% and 5%; when serpentine is present 65-80 wt%, relative errors are ~5 % to ~6% (Hamilton et

al., 2018; Turvey et al., 2018a). In the present study, the XRD abundance of brucite and serpentine in the tailings were reported with the relative uncertainty (Table 2.1). XRD abundance of the hydrotalcite (pyroaurite) was not reported because the sample consists of 100% pyroaurite. Thermogravimetric analysis (TGA) was used to verify the mineral abundance of brucite by measuring the mass of water loss as a function of temperature (Table 2.1). Bulk BET surface areas of each starting material were determined by the multi-point BET method with N<sub>2</sub> gas absorption using a Quanta chrome Autosorb-1 surface area analyzer. A Malvern Mastersizer 2000 laser diffraction particle-size analyzer was used to determine particle-size distributions for each of the samples and their unwashed precursors. A suspension of each sample in deionized water was sonicated prior to and during analysis to minimize particle clumping. Major element oxide compositions of the starting materials were determined using X-ray fluorescence spectroscopy (XRF; Table 2.2) at ALS Global Laboratories, North Vancouver, British Columbia, using lithium borate fusion digestion.

Table 2.1 Table of sample characterization including results from XRD mineral abundance, TGA bruciteabundance, particle grain size, and BET reactive surface area.

Phase Abundance (wt%)	Natural Brucite Sample	Quartz Sample	Swift Creek Serpentinite	GK-PK21	<b>BD-FPCOM</b>
Serpentine (Lizardite)	4.20±0.12	-	90.29±4.8	43.00±2	77.00±3
Phlogopite	-	2.49	3.54±0.2	17.91	-
Clinochlore	-	-	-	12.32	-
Brucite	79.50±1.5	-	$1.76 \pm 1.6$	$1.50{\pm}1.4$	$10.50 \pm 2.5$
Diopside	-	-	-	3.31	-
Dolomite	6.26	-	-	0.96	-
Quartz	0.13	97.51	0.57	1.14	-
Spinel	-	-	-	1.66	6.40
Orthoclase	-	-	-	0.74	-
Albite	-	-	-	2.37	-
Andradite	-	-	-	8.51	-
Grossular	-	-	-	1.69	-
Enstatite	-	-	-	0.79	-
Magnesite	5.51	-	3.83	-	-
Pyroaurite	0.20	-	-	-	-
Forsterite	-	-	-	-	4.10
Hydromagnesite	5.46	-	-	-	-
Total	100.00	100.00	100.00	100.00	100.00
Grain size d(0.9) um	79	298	190	97	76
TGA (brucite wt%)	-	-	-	0.1	8.4
$A_{BET} (m^2 g^{-1})$	4.15	0.13	18.51	9.36	3.84

Sample ID	SiO <sub>2</sub> %	Al <sub>2</sub> O <sub>3</sub> %	Fe <sub>2</sub> O <sub>3</sub> %	CaO %	MgO %	Na <sub>2</sub> O %	K2O %	
Brucite	3.49	0.41	0.93	1.97	59.28	0.07	0.01	
BrQtz mix	89.64	0.29	0.16	0.19	5.58	< 0.01	0.07	
Serpenti ne	38.80	0.58	7.46	0.35	37.84	0.05	0.12	
GK- PK21	38.74	3.57	7.46	7.24	28.77	0.59	1.29	
BD- FPCOM	34.26	0.16	9.625	0.02	41.92	0.065	<0.01	
Sample ID	Cr2O3 %	TiO2	MnO %	P <sub>2</sub> O <sub>5</sub> %	SrO %	BaO %	LOI %	Total %
Brucite	< 0.01	0.01	0.04	0.05	< 0.01	0.01	33.30	99.55
BrQtz mix	< 0.01	0.02	0.01	0.01	< 0.01	< 0.01	3.82	99.78
Serpenti ne	0.24	0.04	0.10	0.02	< 0.01	0.01	13.38	98.97
GK- PK21	0.22	0.63	0.13	0.23	0.04	0.095	10.65	99.64
BD- FPCOM	0.55	< 0.01	0.11	0.002	< 0.01	< 0.01	12.9	99.61

 Table 2.2 Table of the bulk chemical composition of tested samples, determined using x-ray fluorescence

 spectroscopy.

# 2.2.2 Experimental methods

Twelve dissolution experiments were conducted using a purpose-built flow-through timeresolved analysis (FT-TRA) module to quantify the labile Mg content as a function of acid type, pH, and mineral composition. The design and experimental protocol used in this study were a modification of the procedure used by De Baere et al. (2015); only the revised features are detailed here (Figure 2.1a). The experimental set up included a Dionex ICS-3000 dual-gradient pump operating at a flow rate of 1.0 mL/min and a Foxy®R1 fraction collector that is connected with entirely metal-free (PEEK) flow tubes. The reaction chamber was assembled using a 25 mm diameter polypropylene Swinnex filter holder (1.2 mL internal volume) containing a 0.2 µm polycarbonate membrane filter (Millipore catalogue #SLLGC13NL). Weighed sample aliquots were loaded into the filter holder and then shaken to distribute the samples evenly. Sample aliquots inside the holder form packed beds structure that may results in a pH gradient during the dissolution process (Figure 2.1b). Such effects were addressed during data processing of the results. The filter holder was mounted vertically between two parallel, remotely controlled solenoid valves and above a 0.2 um syringe filter (diameter: 13 mm). The syringe filter provided a secondary filtration to prevent fine particulates from clogging the polyetheretherketone (PEEK) tubes. Inlet solution (eluent) flowed through the top solenoid valve, the 1.2 mL reaction chamber, the membrane filter, and then the lower solenoid valve. Polytetrafluoroethylene (PTFE) sealant tape was wrapped around the threading on the screw-fitting of the filter holder to prevent any potential leaks that could occur due to pressure build-up inside the reaction chamber. The dissolution experiments were performed at room temperature and pressure (21–22°C, 1.013bar).

Four types of acids were used to prepare the inlet fluid (eluent) solutions used in this study: carbonic (H<sub>2</sub>CO<sub>3</sub>, 10%CO<sub>2</sub> compressed gas, Praxair), hydrochloric (HCl: ACS Reagent Grade, Sigma-Aldrich Corporation), phosphoric (H<sub>3</sub>PO<sub>4</sub>: ACS Reagent Grade, Sigma-Aldrich Corporation) and nitric (HNO3: Trace Metal Grade, Fisher Scientific International, Inc.). The acids were added to deionized water to obtain a solution of the desired pH. Solutions in equilibrium with CO<sub>2</sub> were prepared by constantly bubbling CO<sub>2</sub> gas (0.039%, 9.99%, 99.99% purity; Praxair) in deionized water at a flow rate of ~200 mL/min throughout the experiment. Gas solutions at 0.04%, 10% and 100% concentration were used to represent aqueous solutions in equilibrium with CO<sub>2</sub> at equivalent partial pressures of 0.0004, 0.1 and 1 bar pCO<sub>2</sub> (see Table 2.4 for gas concentration in ppm, %) The solution at 1 bar  $pCO_2$  is in equilibrium with pure  $CO_2$  gas. The solution at 0.1 bar  $pCO_2$  corresponds to the flue gas  $CO_2$  concentration from a power plant that uses either coal or natural gas as fossil fuel (Sanna et al., 2014; Songolzadeh et al., 2014; Zevenhoven et al., 2008), while the solution at 0.0004 bar pCO<sub>2</sub> represents the CO<sub>2</sub> concentration in the atmosphere. Eluent solutions were equilibrated for a minimum of 24 hours before the start of each experiment to ensure that the pH stabilized near the expected values (pH = 5.60, pH = 4.41, and pH = 3.89) for the solutions at 0.0004, 0.1 and 1 bar pCO<sub>2</sub> based on geochemical modelling using PHREEQC (Parkhurst and Appelo, 2013).



Figure 2.1 Schematic diagram of the experimental set-up and detailed view of the flow-through time-resolved analysis (FT-TRA) experimental apparatus; (a) Schematic illustration of the flow-through system; (b) a detailed view of the pH gradient created by the 'packed-bedded' sample inside the filter reactor.

The outlet fluid (effluent: 13 mL sample volume) was intermittently collected over 13 min periods and at 30 minutes to 2 hours intervals using a Foxy®R1 fraction collector in 15 mL polypropylene tubes; otherwise, the effluent was pumped into a waste basin. The aqueous samples were acidified with 15 M ultra-pure HNO<sub>3</sub> and stored at ~4 °C for no more than six days prior to analysis. All experimental conditions are summarized in Table 2.3. After each experiment, the minerals solids were preserved, dried overnight, and weighed for further characterization. The experiment duration ranged between 70 and 120 hours. Data quality assurance and quality control (QAQC) were performed by comparing the pH measured manually and that measured using the inline pH meter, together with performing charge balance calculations based on the geochemistry of the effluent solution. Mass balance calculations were also conducted based on the consumption of the solid sample (refer to Appendix A and B for details); only experiments that passed QAQC were analyzed further.

Experiment no.	рН	Acid type	Sample(s)	Duration (hours)	Sample mass (mg)	Mass of final solids (mg)	Mg wt% dissolved
19	4.40 <sup>a</sup>	H <sub>2</sub> CO <sub>3</sub>	10%Brucite 90%Quartz	100.00	501.01	456.30	102.00
12	4.40	HCl	10%Brucite 90%Quartz	107.00	500.00	473.00	40.00
8	4.40	HNO <sub>3</sub>	10%Brucite 90%Quartz	70.00	508.00	472.80	35.00
16	4.40	H <sub>3</sub> PO <sub>4</sub>	10%Brucite 90%Quartz	105.00	503.90	482.00	35.00
10	4.40 <sup>a</sup>	H <sub>2</sub> CO <sub>3</sub>	Serpentine	78.00	484.00	467.00	4.50
13	4.40	HCl	Serpentine	103.00	502.30	480.10	3.00
14	4.40	HNO <sub>3</sub>	Serpentine	99.00	504.00	486.50	2.30
18	4.40	H <sub>3</sub> PO <sub>4</sub>	Serpentine	100.00	502.30	480.10	5.00
20	4.40 <sup>a</sup>	H <sub>2</sub> CO <sub>3</sub>	<b>BD-FPCOM</b>	102.00	504.20	410.00	27.00
22	4.40 <sup>a</sup>	H <sub>2</sub> CO <sub>3</sub>	GK-PK21	73.00	509.00	470.60	6.00
26	3.90 <sup>b</sup>	H <sub>2</sub> CO <sub>3</sub>	Serpentine	76.00	504.00	453.60	5.00
27	5.62 °	H <sub>2</sub> CO <sub>3</sub>	Serpentine	122.00	503.00	471.00	2.00
28	4.40	H <sub>2</sub> CO <sub>3</sub>	Hydrotalcite	100.00	501.01	456.30	102.00

Table 2.3 Summary of experimental conditions and total wt% of Mg dissolved. All the experiments were performed at 25°C, 1.013 bar.

<sup>a b c</sup> The eluent solution used in the experiments was 0.001 M NaCl in equilibrium with (a) 0.1 bar pCO<sub>2</sub>, (b) 1 bar pCO<sub>2</sub>, and (c) 0.0004 bar pCO<sub>2</sub>. The flow rate was set to 1 mL/minute for all experiments.

Table 2.4 CO<sub>2</sub> gas concentration unit conversion (ppm, % and bar)

Unit	CO <sub>2</sub>	CO <sub>2</sub>	CO <sub>2</sub>	
	<b>Concentration1</b>	Concentration2	Concentration3	
ррт	400	1000	1000000	
bar	0.0004	0.1	1	
%	0.04	10	100	

## 2.2.3 Analytical methods

The eluent and reacted effluent pH were continuously measured (approximately once every 5 seconds) using Bio-Rad DuoFlow inline electrodes calibrated in buffer solutions (pH = 4.00, 7.00,10.00) before and after each experiment. The linear drift of the pH measurement was monitored based on pH electrode calibrations before and after the experiment. One electrode is used per experiment, and a total of three electrodes were used in rotation. The measurement errors were considered negligible if the drift between successive calibrations were within the measurement uncertainty of the electrode (<0.05 pH units). Manual pH measurements of backup samples were made for data QAQC using a Thermal Orion 4-Star Plus Portable pH meter with a measurable pH range between -2 to 19 and precision of  $\pm 0.002$ , as well as a Thermal Orion 9170BN 3-in-1 pH/automatic temperature compensation probe with a pH detection range from 0 to 14. Effluent solutions were analyzed for Al, Ca, Fe, K, Mg, Na and Si concentrations using a Varian 725-ES inductively coupled plasma optical emission spectrometer (ICP-OES) at the Department of Earth, Ocean and Atmospheric Sciences, University of British Columbia. The detection limits of the individual elements are reported in Table 2.5. Calibration standards were prepared by diluting concentrated QCS-27 ICP 27 element Quality Control Standards to concentrations of 0.1 ppm, 0.5 ppm, 0.7 ppm, 1 ppm, 5 ppm, 10 ppm, 15 ppm, 20 ppm, and 30 ppm. The relative error for each analytical run was calculated by formulating a linear relationship based on 7 out of the 9 standards to compute the concentration of the other two standards. The average difference between the calculated concentration and measured concentration was used as the average relative uncertainty for each analysis and are reported in Table 2.6.

Element	Al	Ca	Fe	K	Mg	Na	Si
Detection limit(ppm)	0.50	0.10	0.30	0.30	0.10	0.20	0.30

Table 2.5 Elemental detection limit of different elements for the ICP-OES

Table 2.6 Calculated relative errors of the Mg concentration measurements from each experiment.

Experiment No.	<b>Relative Error</b>
19	7.6%
12	2.4%
8	7.3%
16	18.0%
10	3.0%
13	17.0%
14	1.4%
18	3.0%
20	3.0%
22	2.0%
26	5.7%
27	6.0%

Sample powders retrieved from the dissolution experiments were analyzed by smear mount XRD analysis. Qualitative XRD data for reacted solids were used to assess the decrease in mineral abundance that had occurred during the dissolution process. Mineral saturation indices ( $\Omega$ ) were calculated using PHREEQC V.3 (Parkhurst and Appelo, 2013) based on the measured aqueous chemistry data together with the mineral solubility data from the Wateq4f database. The saturation index  $(\Omega)$  is a useful quantity to determine whether the water is saturated, undersaturated, or supersaturated with respect to the given mineral ( $\Omega < 0$ , undersaturated;  $\Omega = 0$ , saturated equilibrium;  $\Omega > 0$ , supersaturated) (Bowman, 1997). Measurements of pH and  $[Mg^{2+}]$  used to

compute mineral saturation state were averaged over 13 minutes of the sample collection interval. A certain level of uncertainty may be introduced because both measurements of pH and  $[Mg^{2+}]$  are not instantaneous, meaning that  $\Omega > 0$  may represent that the mineral is close to but not yet approached supersaturation. The mineral dissolution rate was calculated based on the Mg concentration of the solution, the mineral BET surface area, and the flow rate, using equation 1 (equation adapted from Daval et al., 2010):

$$R_{Mg \ (mol \ Mg \ m^{-2}s^{-1})} = \frac{r_f \Delta_{[Mg]}}{\eta_{Mg} A_{BET} m_0}$$
 Eq. 1  
$$R_{Mg \ (mol \ Mg \ g^{-1}s^{-1})} = \frac{r_f \Delta_{[Mg]}}{\eta_{Mg} m_0}$$
 Eq. 2

where  $R_{Mg}$  is the reaction rate based on [Mg] (mol m<sup>-2</sup> s<sup>-1</sup>),  $r_f$  is the flow rate (L s<sup>-1</sup>),  $\Delta_{[Mg]}$  is the difference between the effluent and the eluent [Mg] (mol L<sup>-1</sup>),  $\eta_{Mg}$  is the mineral stoichiometric coefficient of Mg, and  $m_0$  is the initial mass of mineral reactant (g).  $A_{BET}$  is the reactive surface area measured using the BET method. Note that the reaction rate is calculated based on the mineral reactive surface area as well as being expressed as per gram of the sample consumed; it is thus reported as both mol Mg m<sup>-2</sup> s<sup>-1</sup> (Eq. 1) and mol Mg g<sup>-1</sup> s<sup>-1</sup> (Eq. 2).

The proton dependent dissolution rate of brucite and serpentine is demonstrated through direct comparison with published rates. Four of the published literature studies on the steady-state dissolution rate of brucite were examined (Jordan and Rammensee, 1996; Palandri and Kharaka, 2004; Pokrovsky and Schott, 2004; Vermilyea, 1969). Of the four studies, Palandri and Kharaka (2004) is a re-evaluation of Vermilyea (1969), where they determined the rate constant (k), activation energy (E) and reaction order (n) for computing brucite dissolution rate at acidic, neutral and basic conditions. The other three are experimental studies that determine the steady-state dissolution rate of brucite over a range of pH. The experimental studies used different brucite

(synthetic and natural) and different techniques to access the reactive surface area for computing reaction rate (Table 2.6). The study of natural and synthetic brucite dissolution in a batch reactor performed by Vermilyea (1969) used calculated surface areas based on particle geometry. Jordan and Rammensee (1996) measured the brucite dissolution rate at pH 2.7 through the movement of the dissolution surface using Scanning Force Microscopy (SFM). Finally, Pokrovsky and Schott, (2004) computed the dissolution rate of brucite using surface area measured via the Krypton absorption multi-point BET method. Direct comparisons of the rates established by various authors achieved several orders of magnitude differences due to normalizing the rates to the reactive surface area of brucite (see Appendix B, Figure 4.3). Reinterpreting these published results and present dissolution rate on a per gram basis minimizes the uncertainty caused by different reactive surface area (see Appendix B, Figure 4.4). Since the multi-point BET method with N<sub>2</sub> gas absorption is used in this study and that the grain size of brucite used in both studies is comparable (53-106um vs 50-100um), the rate from Pokrovsky and Schott (2004) is reinterpreted using the reactive surface area of the brucite in this study for comparison. The bulk stoichiometric reaction rate of serpentine at pH 4.4 is adapted from Thom et al., (2013) and is compared with the serpentine reaction rate in HCl and HNO<sub>3</sub> directly.

Authors	Brucite Source	$A_{BET}$ (m <sup>2</sup> /g)	Powder size (um)	Reactor Type	T (°C)	рН
Vermilyea (1969)	Natural	0.13	10 - 30	stirred batch reactor	25.0	1 - 5
Jordan and Rammensee (1996)	Natural	-	-	SFM	25.0	2.70
Pokrovsky and Schott (2004)	Synthetic	0.204 ±0.01 - 0.120±0.008	50 -200	mixed-flow reactor	25.0	2 - 12

Table 2.7 Summary of conditions of brucite dissolution experiment reported in the literature.

## 2.3 Results

### **2.3.1** Dissolution kinetics experiments

Flow-through mineral dissolution experiments provide a means of determining the reactivity by measuring the rate of cation (i.e.,  $Mg^{2+}$ ) release. Results from brucite and serpentine dissolution are plotted in Figure 2.2, where plot symbols indicate the saturation state of the solution with respect to the dissolved mineral. As shown in Figure 2.2, brucite has a reaction rate that is two to three orders of magnitude faster than the serpentine. For brucite, the reaction rate in the CO<sub>2</sub> equilibrated solution  $(\sim 10^{-7} \text{ mol Mg m}^{-2} \text{ s}^{-1})$  is significantly higher than that for the other acid types  $(\sim 10^{-9} \text{ mol Mg m}^{-2} \text{ s}^{-1})$ <sup>1</sup>) (Figure 2.2). Brucite solubility varies significantly throughout the experiments. Measurements of [Mg<sup>2+</sup>] and pH used for modelling brucite saturation sate in PHREEQC were not instantaneous and may not reflect the saturation state at the exact time step. Brucite seems to have approached supersaturation ( $\Omega$ >0) during the early stages of brucite dissolution in HCl, HNO<sub>3</sub>, and H<sub>3</sub>PO<sub>4</sub>. In contrast, brucite reaction in solution at 0.1 bar pCO<sub>2</sub> remained consistently undersaturated due to lower consumption of H<sup>+</sup> (low pH) and showed a rapid decline in reaction rate beginning after 30 hours. The XRD data revealed no measurable brucite in the post-experimental sample, and the total sample mass loss, calculated from the cumulative  $[Mg^{2+}]$  in the effluent, matched the proportion of brucite in the unreacted sample. During the first 30 hours of brucite reaction, dissolution rates in HCl, HNO<sub>3</sub> are faster than the rate in H<sub>3</sub>PO<sub>4</sub>, after which the rates converge (Figure 2.2). Pokrovsky and Schott (2004) brucite steady-state dissolution rate at pH 4.4 is 2.75×10<sup>-9</sup> mol Mg m<sup>-2</sup> s<sup>-1</sup>, and the rate from Palandri and Kharaka, (2004) is 3.54×10<sup>-9</sup> mol Mg m<sup>-2</sup> s<sup>-1</sup> as plotted in Figure 2.2, which is comparable with the rate of brucite dissolution in HCl, HNO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub> after 30 hours of dissolution. Brucite dissolution rate in solution at 0.1 bar pCO<sub>2</sub> is higher than the published rates by

more than one order of magnitude. The reaction rate in  $H_3PO_4$  agrees with the rate determined by both Palandri and Kharaka, (2004), and Pokrovsky and Schott (2004) demonstrate steady-state dissolution of brucite (Figure 2.2).



Figure 2.2 Reaction rate (mol Mg m<sup>-2</sup> s<sup>-1</sup>) of brucite and serpentine in HCl, H<sub>3</sub>PO<sub>4</sub>, HNO<sub>3</sub> and solution at 0.1 bar pCO<sub>2</sub> as a function of time. The state of solution saturation with respect to brucite and serpentine is represented using data symbols (see legend). The brucite steady-state dissolution rates at a pH 4.4 are from Pokrovsky and Schott, (2004) (dashed red line) and Palandri and Kharaka, (2004) (dashed grey line). The serpentine steady-state rate of dissolution is adapted from Thom et al., 2013 (dashed blue line). \*Measurement error are smaller than the plotted symbols.

In the serpentine experiments, after 30 hours, dissolution rates in the  $CO_2$  equilibrated solution and  $H_3PO_4$  were comparable with each other and were around two times higher than the rates in the other acids (Figure 2.2). The effluent solution remained strongly undersaturated in all the serpentine dissolution experiments, as indicated by plot symbols (Figure 2.2). The published steady-state serpentine dissolution rate at pH 4.4 determined by Thom et al., 2013, is 1.03×10<sup>-11</sup> mol Mg m<sup>-2</sup> s<sup>-</sup> <sup>1</sup>, which is comparable with the serpentine reaction rate in HCl and HNO<sub>3</sub> after 20 hours, demonstrating that serpentine dissolution is proton dependent. Both HCl and HNO3 are strong acids that fully dissociated and release H<sup>+</sup>, Cl<sup>-1</sup> and NO<sub>3</sub><sup>-</sup> upon dissolution, meaning that only protons can activate the dissolution. Results from serpentine dissolution in solutions with CO<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub> are about double the rate measured by Thom et al., 2013 using HCl (Figure 2.2). Moreover, the measured effluent Mg:Si ratio (~5 to ~1.79) is higher than the stochiometric Mg:Si ratio (1.45) in all serpentine dissolution experiments. The stochiometric Mg:Si ratio was determined based on the bulk geochemical composition of the serpentine sample (Figure 2.3) (Table 2.2). The simultaneous drop in the reaction rate and Mg:Si ratio indicates that the serpentine dissolution was approaching stoichiometric and that Mg<sup>2+</sup> was preferentially leached relative to Si<sup>4+</sup>. The cumulative Mg<sup>2+</sup> released from serpentine dissolution in H<sub>3</sub>PO<sub>4</sub> was ~5% of the total compared to 4%, 2.75%, and 2.5% leached in solution at 0.1-bar pCO<sub>2</sub>, HCl, and HNO<sub>3</sub>, respectively (Figure 2.3). Serpentine dissolution in H<sub>3</sub>PO<sub>4</sub> maintained the highest Mg/Si compared to that in the effluent from serpentine dissolution in solution with CO<sub>2</sub>, which was the lowest and attained an Mg/Si of 1.74 at the end (Figure 2.3).

In general, serpentine dissolution behaviors in the four acid types were similar to that of brucite except that the rates were approximately three orders of magnitude slower (Figure 2.4). As mentioned earlier, a pH gradient will form across the packed-bed structure of the pulp samples inside the flow-through cell with time. The x-axis shows the average proton concentration in the packed bed reactor expressed as pH values. As shown in Figure 2.4, the effluent pH started high (~4.7) before dropping slowly back to 4.6-4.5. At a given pH, the reaction rate of brucite in the  $CO_2$  equilibrated solution was much higher than the rate in other acid types and the rate at steady-state.
Brucite dissolution rates in HCl, HNO<sub>3</sub>, and H<sub>3</sub>PO<sub>4</sub> were faster than the rate at steady-state near the beginning of the experiment but converged to the published rates near the end (Figure 2.4). Serpentine dissolution behaved similarly to brucite in that the reaction rates in solutions at 0.1 bar pCO<sub>2</sub> was much higher compared to the rates in H<sub>3</sub>PO<sub>4</sub>, HCl and HNO<sub>3</sub> (Figure 2.4). In the end, effluent pH in H<sub>3</sub>PO<sub>4</sub> remained at 4.7, while the pH in HCl and HNO<sub>3</sub> decreased to around 4.5 (Figure 2.4).



Figure 2.3 Evolution of aqueous Mg:Si ratio (left axis) and the fraction of Mg<sup>2+</sup> reacted (%) (right axis) with time during serpentine dissolution in HNO<sub>3</sub>, HCl, H<sub>3</sub>PO<sub>4</sub> and solution at 0.1 bar pCO<sub>2</sub>. The stochiometric Mg: Si molar ratio of the serpentine is 1.45±0.0056, indicated by the orange line.



Figure 2.4 Reaction rate (mol Mg m<sup>-2</sup> s<sup>-2</sup>) of brucite and serpentine in HCl, H<sub>3</sub>PO<sub>4</sub>, HNO<sub>3</sub> and solution at 0.1 bar pCO<sub>2</sub> as a function of the average [H<sup>+</sup>] in the packed bed reactor expressed as pH. The state of solution saturation with respect to brucite and serpentine is represented using data symbols (see legend). The brucite steady-state dissolution rates from pH 4 to 5 are from Pokrovsky and Schott, (2004) (dashed red line) and Palandri and Kharaka, (2004) (dashed grey line). The steady-state serpentine rate of dissolution of the same pH range is from Thom et al., 2013 (dashed blue line).

\*Measurement errors are smaller than the plotted symbols.

In the serpentine experiments using solutions at various pCO<sub>2</sub>, serpentine dissolution in solutions saturated with 1 bar pCO<sub>2</sub> are the fastest compared to the rates in solutions saturated with air and 0.1 bar pCO<sub>2</sub> (Figure 2.5). The effluent Mg:Si ratio from serpentine reactions in solutions at various pCO<sub>2</sub> all remained higher than the stoichiometric value (Figure 2.6). The cumulative Mg<sup>2+</sup> amount dissolved in solution at 1 bar pCO<sub>2</sub> is ~5% of the total Mg<sup>2+</sup> compared to only 1% in solution at 0.0004 bar pCO<sub>2</sub> (Figure 2.6).



Figure 2.5 Reaction rate (mol Mg m<sup>-2</sup> s<sup>-1</sup>) versus time of serpentine in solutions at 25°C, 0.0004, 0.1 and 1 bar pCO<sub>2</sub>.



Figure 2.6 Evolution of aqueous Mg:Si ratio (left axis) and the fraction of Mg<sup>2+</sup> reacted (%) (right axis) with time. Data are from serpentine experiments using solutions with 0.0004 bar, 0.1 bar and 1 bar pCO<sub>2</sub>. The stochiometric Mg: Si molar ratio of the serpentine is 1.45±0.0056, as indicated by the orange line.

# 2.3.2 Dissolution rate and mineralogy

Serpentine and brucite dissolution rates are compared to those of hydrotalcite and olivine in Figure 2.7. The rates are compared in units of mol Mg  $g^{-1}$  s<sup>-1</sup> because normalizing to mass can avoid the significant uncertainty brought by the differences in mineral reactive surface area (Figure 2.7). For samples with similar grain sizes, the log dissolution rate of forsterite in mol Mg m<sup>-2</sup> s<sup>-1</sup> is higher than chrysotile by more than two orders of magnitude. However, when comparing rates in mol Mg  $g^{-1}$  s<sup>-1</sup>, the rate of chrysotile dissolution become faster. Since the ultimate goal of this study is to estimate the potential of carbon sequestration over a certain mass of tailings, the dissolution rate of different minerals and tailings is compared on in mol Mg g<sup>-1</sup> s<sup>-1</sup>. The reduction of sample mass was considered when computing the dissolution rate and showed trends of decreasing with time. The olivine dissolution data was adapted from Carrol et al. (in prep) for comparison. Of the four minerals tested, brucite dissolved the fastest and experienced full dissolution. The hydrotalcite dissolution results exceeded 70% consumption of total Mg<sup>2+</sup>, demonstrating a slower but comparable reaction rate to that of brucite (Figure 2.7). The hydrotalcite reaction rate dropped to  $10^{-9}$  mol Mg g<sup>-1</sup> s<sup>-1</sup> near the end of the experiment, representing uncertainties of phases present in the remaining mass fraction. The rate of serpentine dissolution was the second slowest among the sampled minerals but was still higher than the olivine dissolution rate by one order of magnitude. The serpentine dissolution rate dropped from around  $10^{-7}$  mol Mg g<sup>-1</sup> s<sup>-1</sup> to  $\sim 10^{-9}$  mol Mg g<sup>-1</sup> s<sup>-1</sup>, during which approximately 4% of the total Mg<sup>2+</sup> was leached (Figure 2.7). The olivine dissolution followed the same trend as serpentine but started at a much lower rate, with less than 1% of the total Mg<sup>2+</sup> dissolved at the end (Figure 2.7).



Figure 2.7 Plot of brucite, olivine, hydrotalcite, and serpentine reaction rate (mol Mg  $g^{-1} s^{-1}$ ) in solution at 25°C, 0.1 bar pCO<sub>2</sub> versus the fraction of Mg<sup>2+</sup> of the total Mg<sup>2+</sup> reacted (%).

# 2.3.3 Dissolution rates of tailings

The tailings sample BD-FPCOM and GK-PK21 have distinctly different mineralogical content. BD-FPCOM contains ~10.5 wt% brucite and ~77 wt% serpentine compared to GK-PK21, which has ~1.5wt% brucite and ~43wt% serpentine. The reaction kinetics of mineral mixtures with various mineral abundance should reflect the integrated reaction rate of individual minerals. More importantly, dissolution rates of real tailings are representative of material with a wide range of grain sizes. To test this, samples of ultramafic tailings were reacted using the same chemical environments as the pure mineral dissolution tests (Figure 2.8). The behavior of the two tailings samples showed three distinct differences:

1) the BD-FPCOM results shows a single-stage reaction, whereas the GK-PK21 showed a twostage reaction; the latter involving a release of ~1% of the total  $Mg^{2+}$  at a fast rate (~10<sup>-8</sup> mol Mg g<sup>-1</sup> s<sup>-1</sup>) followed by an additional 4% as the rate dropped to ~10<sup>-9</sup> mol Mg g<sup>-1</sup> s<sup>-1</sup> (Figure 2.8);

2) the BD-FPCOM, which contains much higher brucite and serpentine contents than the GK-PK21, reacted almost an order of magnitude faster during the first 60 hours of the experiment; and

3) The dissolution of the BD-FPCOM resulted in a greater total amount of leached  $Mg^{2+}$ .

The brucite and serpentine dissolution rates in the same chemical environment were compared with the tailings dissolution rate to observe the effect of mineralogy on the dissolution kinetics of the tailings (Figure 2.8). A rapid drop in reaction rate after ~40 hours of the experiment can be observed for both the brucite and the BD-FPCOM samples since both samples contain ~10wt% of brucite (Figure 2.9). The GK-PK21 dissolution experiment results have a nearly identical trend to the serpentine dissolution, which exhibited a rapid drop in reaction rate during the first 10 hours, after which it remained at a stable dissolution rate for the remaining 70 hours (Figure 2.9).

Noticeably, both BD-FPCOM and GK-PK21 attain similar reaction rates after 60 hours of reaction, after which the dissolution rate for the nickel tailings falls (Figure 2.9).



Figure 2.8 Plot of reaction rate (mol Mg g<sup>-1</sup> s<sup>-1</sup>) versus fraction reacted% of the BD-FPCOM and the GK-PK21 in solutions at 25°C and 0.1 bar pCO<sub>2</sub>.



Figure 2.9 Reaction rate (mol Mg m<sup>-2</sup> s<sup>-1</sup>) versus time of the BD-FPCOM, the GK-PK21, serpentine and brucite in solutions at 25°C and 0.1 bar pCO<sub>2</sub>.

#### 2.4 Discussion

One of the limitations of mineral carbonation and low-cost carbon sequestration strategies is accessing cations through mineral dissolution under atmospheric conditions. Based on the results from all the flow-through experiments, the reactivity (i.e. labile Mg content) of ultramafic tailings seems to be highly dependent on their mineralogical composition and the surrounding geochemical environment. Conventional mineral dissolution experiments have typically focused on determining the long-term dissolution rate of minerals at steady-state; however, such an approach often neglects the incongruent dissolution rate, which is typically transient and faster, especially during silicate mineral dissolution (Assima et al., 2012; Daval et al., 2013; Krevor and Lackner, 2011; Luce et al., 1972; Martinez et al., 2014; Power et al., 2013; Rimstidt and Olsen, 2012; van Grinsven et al., 1992). For carbon sequestration at atmosphere conditions, determining and understanding the labile fraction of the total Mg<sup>2+</sup> means putting research focus on the transient, early-stage dissolution rate of various minerals. The experimental results presented herein demonstrate how the transient reaction rate of Mg-silicates and bulk dissolution rate of Mg-hydroxides varies among different mineral phases and chemical conditions. It is clear from our results that the labile Mg of ultramafic tailings is fundamentally controlled by mineral variability and geochemical environment.

# 2.4.1 Labile Mg

Accurate characterization of reactivity is significant for estimating the accessible carbon sequestration capacity of ultramafic mine tailings. The experimental results obtained in this study enable estimations to be made by defining reactivity in terms of labile Mg. We define labile Mg as Mg<sup>2+</sup> that can be rapidly leached at ambient pressure and temperature conditions. This definition includes two components: a threshold rate and a corresponding fraction of Mg<sup>2+</sup> that can be leached at or above this rate. Defining labile Mg, thus, become more complicated than simply using transient and steady-state dissolution conditions for different minerals as the steady-state reaction of some minerals may be significantly faster than even the transient dissolution rate of other minerals. Furthermore, the decline in reaction rate as some minerals transition from transient to steady-state reactions may mean that some minerals only have a portion of their total Mg<sup>2+</sup> be labile. More importantly, the labile portion of the Mg<sup>2+</sup> can increase or decrease under the effects of different acid strengths and types. To further minimize the effect from physical properties such as grain size and available surface area on the dissolution rate of natural minerals and ultramafic tailings, we normalize dissolution rate to mass (mol Mg g<sup>-1</sup> s<sup>-1</sup>) before comparing. Additionally, we perform experiments on real tailings and determine their dissolution rates based on sample mass and BET surface area. Even though the particle size distribution of tailings is determined by the milling process and type of ore, having representative dissolution rate measurements of real tailings allows us to use labile Mg for defining the reactivity of tailings for mineral carbonation.

Drawing this delineation between labile and non-labile Mg is necessary for quantifying reactivity and applying mineral carbonation technique at industrial mine sites. We choose to make the labile Mg dissolution rate to be  $\sim 10^{-8}$  mol Mg g<sup>-1</sup> s<sup>-1</sup> as this is the steady-state dissolution rate of pure brucite between pH=3 and pH=5 (Figure 2.10). The steady-state rate of brucite dissolution is

used because brucite represents the most reactive mineral source of Mg<sup>2+</sup> commonly found in ultramafic deposits. The range of pH from 3 to 5 is chosen because this represents the acid conditions of water that are in equilibrium with pure CO<sub>2</sub> gas and air (the likely minimum and maximum acidic conditions that are likely in a low-cost carbon sequestration scenario). Because the value of  $\sim 10^{-8}$  mol Mg g<sup>-1</sup> s<sup>-1</sup> is dependent on the mass of the reacting sample, this value scales with the mass of reacting labile Mg. For example, for a sample with labile Mg that is only 1% of the total Mg, complete dissolution within the same time frame will be achieved at a dissolution rate that is 100 times slower (~ $10^{-10}$  mol Mg g<sup>-1</sup> s<sup>-1</sup>). Minerals that dissolve at a rate higher than  $10^{-8}$  mol Mg  $g^{-1}$  s<sup>-1</sup> and can dissolve 100% of the Mg<sup>2+</sup> in their crystal structure are considered highly reactive, with 100% labile Mg. Conversely, minerals that dissolve at rates lower than 10<sup>-11</sup> mol Mg g<sup>-1</sup> s<sup>-1</sup> have 0.1% labile Mg cannot contribute to effective mineral carbonation. The rationale for defining labile Mg is fundamental for the discussions on variables affecting labile Mg and the implication for the mining industry. Figure 2.10 plots the dissolution rate (measured in mol Mg  $g^{-1}$  s<sup>-1</sup>) and fraction reacted (% total Mg), for all of the experiments described in Table 2.3. The two dashed black lines represent the limit of the labile Mg rate and labile Mg content of the experiments. In Figure 2.10, we see that the results of the various experiments vary significantly and see how many experiments either transition from labile to non-labile Mg release or approach this boundary. For example, brucite is capable of leaching 100% of the total Mg<sup>2+</sup> at a rate higher than 10<sup>-8</sup> mol Mg g<sup>-</sup> <sup>1</sup> s<sup>-1</sup> in solutions at 0.1 bar pCO<sub>2</sub>. Serpentine, on the other hand, releases only 4% Mg<sup>2+</sup> (Figure 2.10). The variation in results depends on the mineralogy of the sample analyzed, as well as the acid strength and acid type used in the dissolution experiment.



Figure 2.10 Plot of reaction rate versus fraction reacted for flow-through experiments conducted for all samples of similar grain size in various chemical conditions. The dashed black lines represent the boundary between labile and non-labile Mg; the upper limit is brucite steady-state dissolution rate in pH=3 solution while the lower limit is the rate in pH=5 solution.

#### 2.4.2 Labile Mg dependence on pH

Dissolution kinetics of minerals have a strong dependence on acid strength that increases with acidity. Serpentine dissolution at higher pCO<sub>2</sub> and lower pH is faster than the rates at lower pCO<sub>2</sub> and higher pH (Figure 2.5). Under more acidic conditions, more Mg<sup>2+</sup> are liberated from the serpentine crystal structure, representing a faster rate of reaction. As plotted in Figure 2.11, serpentine labile Mg content in solution at 1, 0.1 and 0.0004 bar pCO<sub>2</sub> are ~5, ~4 and ~1% of the total Mg<sup>2+</sup> content. The dependence of serpentine and brucite steady-state dissolution rate on acid strength is well established (Béarat et al., 2004; Harrison et al., 2013c; Jordan and Rammensee, 1996; Lin and Clemency, 1981; Palandri and Kharaka, 2004; Pokrovsky et al., 2009, 2005; Vermilyea, 1969). Brucite dissolution is near steady-state, and at a rate that is faster than the cutoff line, defining labile Mg (Figure 2.10). Labile Mg in brucite is, therefore, 100%. Serpentine, on the other hand, represents the transient, incongruent dissolution. Since most earlier studies focused on establish silicate reaction mechanisms and rate laws at steady-state, the main results of this study shed light on reaction mechanisms that describe the early-stage dissolution process. The non-steadystate behavior of serpentine dissolution can be characterized in terms of the aqueous Mg:Si ratio (Figure 2.3, Figure 2.5). Results from the dissolution experiments suggest that the stoichiometry of incongruent serpentine dissolution correlates negatively with pH. Labile Mg content of serpentine reacting in solution at pH=3.89 is the highest compared to that in solution at pH=4.4 and pH=5.68 (Figure 2.11). This further evidence that the incongruent, transient dissolution rate of serpentine can be accelerated with elevated pCO<sub>2</sub> because lower pH results in thicker mineral leached layer at stead-state. As noted by Goff and Lackner (1998), due to the relatively wide-spread occurrence and high Mg content, Mg-silicates represents an appealing target for CO<sub>2</sub> sequestration (Wilson et al.,

2009b). Minerals in ultramafic tailings that are exposed to more acidic conditions will release more labile Mg and have higher capacities for carbon sequestration.



Figure 2.11 Labile Mg content (%) of serpentine as a function of pH.

# 2.4.3 Labile Mg dependence on acid types

Mineral reactions that proceed via the mechanism of dissolution are often significantly affected by the composition of aqueous solutions. This was evident in our experimental results where it can be observed that the acid type controlled the dissolution kinetics of both brucite and serpentine, demonstrating that acids with ligands promote mineral dissolution (Figure 2.2). For experiments carried out in solutions equilibrated with elevated pCO<sub>2</sub>, enhanced brucite and serpentine dissolution rate was observed with respect to the baseline H<sub>2</sub>O-HCl and H<sub>2</sub>O-HNO<sub>3</sub> solution, which can be attributed to the kinetic-promoting effect of HCO<sub>3</sub><sup>-</sup> ligands. For experiments carried out in phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) solutions, a moderate increase in reaction rate is observed for serpentine but not for brucite (Figure 2.2). Similar to protons, inorganic ligands (HCO<sub>3</sub><sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>) exert their influence by reacting directly with hydroxyl ions on mineral surfaces (Vermilyea, 1969).

Protons and ligands promote the dissolution of brucite in parallel; their effects are additive (Harrison et al., 2013b). Ligand-promoted dissolution of brucite was already examined and demonstrated in Pokrovsky et al. (2005). Results from Pokrovsky et al. (2005) show that inorganic ligands that form protonated ions (e.g.,  $HCO_3^-$  and  $H_2PO_4^-$ ) at neutral to weakly alkaline pH, promote dissolution, whereas those that form deprotonated ions (e.g.,  $CO_3^{2-}$  and  $PO_4^{3-}$ ) may inhibit dissolution. Pokrovsky et al. (2005) also reported that  $H_2PO_4^-$  is more effective than  $HCO_3^-$  for promoting brucite dissolution at neutral (pH=7.5±0.3) to alkaline pH (pH=8.5 and 9.6). However, evaluation of this is not straightforward in this study because the H<sub>3</sub>PO<sub>4</sub> concentration and pH are not in the same range to evaluate the effectiveness. Carbonic acid results in faster brucite dissolution than phosphoric at the acidic effluent conditions (pH=4-5) achieved in this study (Figure 2.4). Table 2.8 distinguishes carbonate and phosphoric ligands in terms of their pKa (a measure of the strength of an acid). Ligands that are more protonated, indicated by higher pKa values, tend to react more

with hydroxyl ions on the mineral surface and promote dissolution. Additionally, a lower pKa value indicates a higher concentration of a ligand at low pH, whereas a higher pKa allows a higher concentration of a ligand under alkaline conditions. The H<sub>2</sub>CO<sub>3</sub> molecule has a lower pKa while  $HCO_3^-$  has a higher pKa than H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, meaning that at pH=4 to pH=5, H<sub>2</sub>CO<sub>3</sub> molecules are more protonated and present in higher number compared to  $HCO_3^-$  and it is more effective for brucite dissolution than H<sub>2</sub>PO<sub>4</sub><sup>-</sup>. Solution pH, thus, exerts a primary control on the behaviour of ligands on enhancing or inhibiting brucite dissolution (Harrison et al., 2013b). H<sub>2</sub>CO<sub>3</sub> and  $HCO_3^-$  are the more effective ligands for enhancing brucite dissolution at acidic pH than H<sub>2</sub>PO<sub>4</sub><sup>-</sup>.

Serpentine dissolution also appears to be accelerated by HCO<sub>3</sub><sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> ligands in a fashion similar to that for brucite (Figure 2.2). Ligands activation has been an overlooked dissolution pathway, especially concerning the incongruent transient stage of serpentine dissolution (Figure 2.2). The activation process is comparable to brucite because the crystal structure of serpentine includes interbedded brucite layers (Turvey et al., 2018b). In Figure 2.5, the dissolution rate measured at elevated pCO<sub>2</sub> is ~5 times greater than that obtained without CO<sub>2</sub> at pH ~4.7 indicating more effective leaching of labile Mg with CO<sub>2</sub>. Labile Mg content of serpentine reaction in HCl, HNO<sub>3</sub>, H<sub>2</sub>CO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub> ranges from 1% to 5%, demonstrating a strong preference for acids with ligands activations. As opposed to serpentine, even though the rate of brucite dissolution varies with acid type, labile Mg content of brucite remains at 100% (Figure 2.10). The transition of the serpentine dissolution rate corresponds to the switch from labile to non-labile Mg. The labile Mg content in serpentine, therefore, varies with acid type because the rate during transient dissolution is higher in solution with ligands. This is relevant to tailings carbonation because serpentine represents a significant proportion of the total carbon sequestration potential in ultramafic tailings. The labile Mg content of serpentine is underestimated based on the effect of protons alone.

 Table 2.8 Chemical formulas of the studied ligands and their acid ionization constants. The pKa's are from

 waterq4f Database in PHREEQC.

Ligand	HCO <sub>3</sub> -	H <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	H <sub>3</sub> PO <sub>4</sub>	HPO4 <sup>2-</sup>	PO4 <sup>2-</sup>
рКа	10.329	6.351	7.21	2.21	12.346	19.553

### 2.4.4 Labile Mg dependence on mineralogy

Mineral dissolution rates vary between minerals and are dictated by the mineral crystal structure. Brucite and pyroaurite dissolve more than one order of magnitude faster than the other tested minerals (Figure 2.7), related to the effects of crystal structures and elemental bonding. Bonds that are essential to the crystal structure (typically, the shortest and strongest bonds) are often ratelimiting for dissolution (Schott et al., 2009). Brucite and pyroaurite are Mg-hydroxide minerals that require the breaking of only the Mg<sup>2+</sup>-OH bond during dissolution. This is different from multioxide minerals such as olivine, serpentine, where numerous metal-oxygen bonds need to be broken, and Si-O bond is the strongest bond there is to break (Béarat et al., 2004; Jarvis et al., 2009; Luce et al., 1972; Pokrovsky and Schott, 2000; Schott et al., 2009). Hydrotalcite dissolves slower than brucite because the dissolution is incongruent, and preferentially releases Mg<sup>2+</sup> while leaving behind a Fe<sup>3+</sup>- enriched residue that increases with pH (López-Rayo et al., 2017). This enriched residue could theoretically limit the extent of reactions during hydrotalcite dissolution and may inhibit the release of Mg<sup>2+</sup> (Turvey et al., 2018b). Furthermore, the dissolution rates of silicates tend to decrease with increasing silica polymerization (Power et al., 2013). Olivine (forsterite-Mg endmember: Mg<sub>2</sub>SiO<sub>4</sub>), is an orthosilicate that is completely unpolymerized and therefore tends to dissolve more rapidly than phyllosilicates such as serpentine on a per gram basis (De Baere et al., 2015; Luce et al., 1972; Martinez et al., 2014; Pokrovsky and Schott, 2004; Rimstidt et al., 2012).

However, in Figure 2.7, serpentine dissolves faster because the mineral has a larger reactive surface area compared to that of olivine. Serpentine is a phyllosilicate with a 1:1 ratio of tetrahedral silicate layers to octahedral brucite layers. Existing studies on serpentine dissolution (Daval et al., 2013) suggest that the rate of serpentine dissolution is initially highly non-stoichiometric due to the preferential release of Mg<sup>2+</sup> from the surface 'brucite-like' sheets. The total Mg<sup>2+</sup> content in the outermost face (the brucite-like sheet) and the four lateral faces of the crystallite are estimated to be around  $2.73 \times 10^{-4}$  mol or 6.2% of the total Mg<sup>2+</sup> in the serpentine sample that weighs 500mg and has a BET surface area of 18.51 m<sup>2</sup> g<sup>-1</sup> (see Appendix B.2 for details). Serpentine has more labile Mg compared to olivine because the surface  $Mg^{2+}$  is the primary source of labile Mg in serpentine, and they are fast-reacting during incongruent dissolution. The congruent dissolution of serpentine starts as soon as the release of surface Mg<sup>2+</sup> from the pristine crystallites is achieved, and the breakdown of the silicate network results in the slow, stoichiometric steady-state rate of dissolution (Daval et al., 2013). The labile Mg content of different mineral phases is, therefore, highly variable. Under the same chemical conditions, the bulk dissolution rate of Mg-hydroxides is several orders of magnitude faster than that of the incongruent, transient dissolution rate of Mg-silicates. The suitability of silicate minerals as carbon mineralization feedstock increases as the number of longer-and, therefore, weaker-more accessible Mg-O bonds in the mineral structure increases (Dove and Czank, 1995). Given the differences in mineral abundance, the labile Mg content of tailings with higher abundances of Mg-hydroxides will be much greater than tailings that contain higher proportions of Mg-silicates.

#### 2.4.5 Labile Mg in ultramafic tailings

The potential of tailings as CO<sub>2</sub> sequestration feedstock arises primarily due to the mineral phases that compose the tailings and is highly dependent on the surrounding geochemical conditions. The labile Mg content of tailings, hence, can be estimated based on their XRD mineral abundance. The brucite abundance in BD-FPCOM ranges from 8 to 13 wt%. Similarly, the XRD brucite content in GK-PK21 varies from 0.1 to 3wt%, meaning that the reactivity of GK-PK21 is much lower due to the low abundance of brucite. The labile Mg content of BD-FPCOM and GK-PK21 in solution at 0.1 bar pCO<sub>2</sub>, as measured using flow-through dissolution, was around 21% and 9%, respectively (Figure 2.10). The labile Mg content estimated using the XRD abundance and the measured labile Mg from reacting brucite, serpentine, and forsterite in solution at 0.1 bar  $pCO_2$ was  $20 \pm 3\%$  and  $6 \pm 3\%$  for BD-FPCOM and GK-PK21, respectively (Table 2.9). Within the measurement error of XRD, a good agreement is achieved between the estimated tailings reactivity, and the labile Mg content determined using the flow-through dissolution experiments. This result demonstrates that the mineralogy exerts a first-order control on the labile Mg content of the tailings. The abundance of brucite is significant for determining the dissolution rate and the labile Mg content of complex ultramafic tailings.

Overall, experimental results demonstrate that the mineral abundance of tailings is one of the most significant aspects that control reactivity. Tailings with a high abundance of reactive minerals such as brucite will have more labile Mg compared to those with a high abundance of less reactive minerals such as serpentine. Factors that have secondary impacts on reactivity include the geochemical environment, which further refines the accuracy of labile Mg content in tailings. Figure 2.12 plots how labile Mg varies for minerals and tailings in solutions at different  $pCO_2$  (i.e. different pH). For carbon sequestration, the fractions of Mg<sup>2+</sup> that are accessible in solution with pure CO<sub>2</sub>

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represents the maximum reactivity and capacity for mineral carbonation. In contrast,  $Mg^{2+}$  that is leachable in solution at equilibrium with air CO<sub>2</sub> represents the minimum reactivity (Figure 2.12). Serpentine and brucite abundance can be used as a first-order estimate of the bulk labile Mg content in ultramafic tailings. However, a more accurate measurement of labile Mg content in tailings requires information on the surrounding chemical conditions (i.e. the CO<sub>2</sub> stream).

	Labile Mg based on brucite abundance (%)	Labile Mg based on serpentine abundance (%)	Estimated labile Mg (%)	Measured labile Mg (%)
<b>BD-FPCOM</b>	17±3	3±0.2	20±3	21
GK-PK21	3.35±3	2.3±0.1	6±3	5

Table 2.9 Table comparing estimated labile Mg with measured labile Mg of the tailings sample.



Figure 2.12 Labile Mg content of minerals and tailings extracted in the time-resolved flow-through analyzer. Labile Mg content measurement for Mount Keith Tailings (MKM) is adapted from Caroll et al., in prep.

## 2.5 Implications

In Figure 2.13, we show in vertical graphs the tonnes of  $CO_2$  can be carbonated per tonnes of tailings per year both in terms of sequestration capacity and mine emissions. The diagram in red represents the emissions signature of two representative mines. One is based on a high volume openpit low grade, disseminated nickel deposit where natural gas is used for electricity. The other one is based on a small, open-pit diamond mine that is located in a very remote area where diesel power is used. The electricity consumption at the diamond mine is a lot less than the nickel because less energy is required for comminution. However, for a small diamond mine that does not need a high degree of comminution, the most significant carbon footprint comes from truck emissions, which is double the nickel mines. The diagrams in blue and green show estimations of the carbon sequestration capacity based on the mineral composition of the tailings and acidic conditions (i.e. concentration of CO<sub>2</sub> gas) (Figure 2.13). The rates of Mg<sup>2+</sup> released per year from brucite and serpentine are multiplied with the weight of tailings (~1 ton) available. Labile Mg in moles of MgO per tonnes rock from brucite and serpentine are summed and converted to grams of CO<sub>2</sub> sequestered per tonnes of rock, assuming mineral carbonation and hydromagnesite  $[Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O]$ formation. The stoichiometric ratio for converting Mg to C is (4/5, 0.8), according to the chemical formula of hydromagnesite. Therefore, the comparisons are made according to the carbon sequestration capacity rather than reactivity. The data on tailings composition and emissions comes from the Mount Keith nickel mine and the Gaucho Kué diamond mine (Wilson et al., 2009). High brucite tailings (84wt% serpentine, 6.6wt% brucite) in the blue diagram is used to represent nickel tailings, and the low brucite tailings (88wt% serpentine, 1.8wt% brucite) in the green graph is typical of both diamond and nickel tailings. Because labile Mg is more abundant in acidic

conditions, the carbon sequestration capacity and rates will be higher if high concentration  $CO_2$  gas streams are available.

The emissions signature varies depending on mine styles and sources (i.e. fleet emissions and electricity generations). More importantly, the carbon footprint is dictated by the type of fossil fuels used and if there is the use of renewable energy. For a nickel mine such as Mount Keith (MKM), the total GHG emissions are typically around 0.035 tons of CO<sub>2</sub> per ton of tailings per year, of which  $\sim 2/3$  comes from electricity generation using natural gas as the power source, and the remainder comes from truck emissions (Vanderzee et al., 2019; Power et al., 2020b). With an averaged tailings composition of around 84 wt% of serpentine and 6.6 wt% of brucite at MKM, we can calculate the labile Mg content of serpentine reaction in atmospheric CO<sub>2</sub>. Together with the reactivity from brucite, the calculated total labile Mg content is sufficient to make this open-pit nickel mine not only carbon-neutral but also carbon negative (Figure 2.13). Similarly, such reactivity can also offer enough capacity to offset the total carbon footprint at a diamond mine, such as Gahcho Kué. The total GHG emissions of Gahcho Kué are higher at around 0.042 tonnes of CO<sub>2</sub> per tonnes of tailings per year, of which  $\sim 3/5$  comes from truck emissions (Figure 2.13). However, electricity generation at the diamond mine by fossil fuel combustion generates concentrated point sources of CO<sub>2</sub>, which can be injected directly into the tailings. The total labile Mg content obtained from reacting to the low-brucite tailings with CO<sub>2</sub> from point source would contribute enough capacity to offset 90% of truck emissions at mines like Gahcho Kué (Figure 2.13).

Therefore, the estimation of the carbon sequestration capacity using labile Mg is highly dependent on the mineral composition of tailings, and the source of  $CO_2$ . The carbon footprint is highly variable at each mine and will dictate the carbon sequestration capacity and rate. Pure  $CO_2$  produces the most acidic environment for extracting labile Mg but is not practical for industrial

applications as it is neither environmentally friendly nor cost-effective. In contrast, the unintentional direct capture of atmospheric CO<sub>2</sub> using mine tailings is at zero cost and helps reduce the CO<sub>2</sub> level in the atmosphere. Recycling of flue gas exhausts (3-20% CO<sub>2</sub>) (Songolzadeh et al., 2014) from power plants located at mines are also desirable as this will help to reduce GHG emissions and minimize carbon tax. Therefore, estimation of tailings' reactivity should use CO<sub>2</sub> emitted from point sources and air as they are more desirable when dealing with real-world applications. Ultramafic mines with a relatively low-brucite content could still potentially be carbon neutral if higher-concentration CO<sub>2</sub> is available. Nevertheless, the rate of CO<sub>2</sub> supply from gaseous CO<sub>2</sub>(g) to the aqueous phase (e.g.,  $H_2CO_3$  or  $HCO_3^-$ ), or the rate of mineral carbonation, can also limit tailings' capacity to capture CO<sub>2</sub>, which will require further testing and investigation.

In conclusion, this study proposed and defined the concept of labile Mg as a means of characterizing the reactivity of ultramafic mine tailings for use in carbon capture and storage. The results from the mineral dissolution studies presented here demonstrate that mineral abundance and geochemical environment have first and second-order controls on the labile Mg content of tailings. The presence of CO<sub>2</sub> can enhance the mineral dissolution kinetics and the labile Mg content of minerals and tailings, and the samples that were investigated show very encouraging results for meaningfully offsetting GHG emissions from ultramafic mine operations. For industrial applications, the incentives for mining companies to explore the potential of using tailings to capture CO<sub>2</sub> could come from taxes on CO<sub>2</sub> emissions. Currently, the provincial government of British Columbia, Canada, imposes a carbon tax of \$35 per tonnes CO<sub>2</sub> on fossil fuel GHG emissions, and this is anticipated to rise to \$50 per tonnes CO<sub>2</sub> by 2021. Sufficient CO<sub>2</sub> sequestration at mine sites can translate the tax on CO<sub>2</sub> emissions into savings of millions of dollars per year. A multi-tiered approach to CO<sub>2</sub> mineralization based on the carbon price and appropriate social and economic

policies are recommended in relation to the implementation of carbon sequestration technology (Power et al., 2020b). Based on the sources of CO<sub>2</sub>, the mine infrastructure, carbon price, operational costs, and the implementation of carbon sequestration technologies, and also the labile Mg content, the feasibility of using ultramafic tailings to sequester CO<sub>2</sub> could be more accurately estimated. Labile Mg avoids the underestimation of ultramafic tailings capacity for mineral carbonation. More importantly, carbon sequestration using mine tailings opens up the opportunity for future ultramafic mining to be carbon-neutral and potential carbon negative.



# Tonnes CO<sub>2</sub> / Tonnes Tailings / Year

Figure 2.13 A conceptual diagram illustrating the carbon sequestration capacity based on emissions signature. CO<sub>2</sub> sequestration capacity is calculated using average mineral abundance data of tailings from the Mount Keith nickel mine and the Gahcho Kué diamond mine. The values of GHG emissions were adapted from the Mount Keith mine and the Gahcho Kué mine to represent emissions signatures of diamond and nickel mines (Power et al., 2020b; Wilson et al., 2009b).

# Chapter 3: Assessing mineral carbonation reactivity using batch dissolution and disk carbonation experiments

# 3.1 Introduction

Climate change and rising atmospheric CO<sub>2</sub> levels have become much debated environmental issues in recent years. Point source emissions of CO<sub>2</sub> from industrialized processes such as power generation, fossil fuel and mining account for much of the increase (Farrelly et al., 2013; IPCC 2018a; Schaefer et al., 2011). Climate change is projected to have severe implications for a variety of different societal and environmental systems in the next 50 years (IPCC 2007, 2018b, 2018a) and thus, reducing GHG emissions is of the utmost importance. One of the strategies that will be necessary to mitigate climate change is through carbon capture, utilization and storage (CCUS) of GHGs such as carbon dioxide (CO<sub>2</sub>). In response, a variety of schemes for the collection and disposal of CO<sub>2</sub> have been investigated recently (Lackner et al., 1995). Carbon sequestration via mineral carbonation (also known as carbon mineralization) has the potential to be implemented at an industrial scale given its high carbon storage capacity (G.T.), and long storage time (millennia) compared to other carbon sequestration strategies (Lackner 2003; Lackner et al., 1995; Lackner et al., 1997; Seifritz 1990; Sipilä et al., 2008). Mineral carbonation involves leaching available cations from certain minerals through dissolution reactions, followed by the binding of these cations with CO<sub>2</sub> to form carbonate minerals. Industrial waste materials like mine tailings are high in reactive surface area as a result of the crushing and grinding during mineral processing and, thus, are ideal for carbon mineralization. Different tailings materials will have different sequestration capacities. Specifically, mine wastes from ultramafic rock-hosted mines producing commodities such as

asbestos, diamond, chromite, and nickel have the highest predicted capacity (Bea et al., 2012; Pronost et al., 2011; Wilson et al., 2009, 2010, 2011; Wilson et al., 2006).

The geochemical framework of the mineral carbonation process includes 1) the natural weathering of Mg-silicate and hydroxide minerals under atmospheric conditions; 2) the dissolution of  $CO_2$  into the water film around the mineral grains and, 3) the precipitation of Mg-carbonate minerals. Dissolution kinetics of silicates at atmospheric conditions is typically orders of magnitude slower than that of hydroxides. Nonetheless, Mg-silicate minerals have the highest abundance in ultramafic rocks and thus, represent the most significant potential source of Mg<sup>2+</sup> for mineral carbonation. In order to enhance the capacity of mineral carbonation, strategies targeted at enhancing silicate mineral dissolution and carbonation at atmospheric conditions are needed to maximize the economic feasibility and potential of mineral carbonation at mine sites.

Studies on various mineral dissolution mechanisms and kinetics are significant for mineral carbonation in mine tailings because not all cations are accessible under atmospheric conditions. If we only target Mg<sup>2+</sup> that is highly reactive and loosely bounded at the mineral surface, we can define mineral carbonation reactivity as labile Mg, which represents carbon sequestration at a desirable rate and capacity. Mineral dissolution in a flow-through reactor was used to define the concept of loosely bound, fast reacting labile Mg and the slower reacting non-labile Mg (Chapter 2). Results show that all Mg<sup>2+</sup> in Mg-hydroxides are labile due to their high reactivity, while Mg-silicates contribute less due to their slow dissolution kinetics. Results from the flow-through dissolution experiments further establish that the rate and amount of labile Mg vary with mineralogy and chemical environment.

The FT-TRA module presented in Chapter 2 for conducting the flow-through dissolution experiments can be challenging to set up and operate. The hardware of the FT-TRA module (a high-

precision gradient pump, the flow-through reactor, solenoid valves and in-line pH electrodes) are costly and require significant maintenance. The module is also prone to pressure build-up and leakage when testing fine-grained materials such as tailings. Alternative experiment protocols that are faster, less expensive and easier to operate are sought for more efficient evaluation. In this chapter, labile Mg content measured using flow-through is compared with that measured using other experimental protocols to validate our definition of labile Mg presented in chapter 2.

One alternative is batch dissolution experiments. Batch reactors are closed-system vessels containing a sample of the minerals and an aqueous solution of known volume. In this chapter, batch dissolution is used for characterizing transient mineral dissolution kinetics and quantifying labile Mg. The reactors were continuously agitated (stirred and shaken) under ambient conditions during the experiments. Magnesium concentration was cumulative rather than time-resolved. Nevertheless, the loss in temporal resolution in conventional techniques is compensated by its time-, resource-, and cost-effectiveness compared to the FT-TRA. Moreover, different agitation methods can be imposed during dissolution to accelerate reaction kinetics. If batch dissolution is valuable for measuring labile Mg content, it will serve as a low-cost and labour-efficient option for assessing mineral carbonation reactivity of mineral and tailings.

A second option is disk-carbonation experiments that measure cation release and carbonate precipitation. Both the batch dissolution and the FT-TRA technique rely on the leachable  $Mg^{2+}$  in aqueous solution to quantify reactivity, and neither one includes the subsequent carbonation reactions as part of the assessment process. Since the precipitation of carbonate minerals is also one of the essential controls of tailings' reactivity, an innovative and advanced methodology, referred to as disk carbonation, is developed to assess the mineral carbonation reactivity of minerals and tailings. The disk carbonation method treats samples under humidified  $CO_{2(g)}$  in a closed

environment and monitors the increase in the solid Mg-carbonate material. This method assesses both the extent of  $Mg^{2+}$  release and the extent of carbonation. In this chapter, both techniques are tested using a subset of samples from chapter 2. The test results and discussions have revealed essential implications for the future advancement of protocols assessing tailings' reactivity for  $CO_2$ sequestration.

# 3.2 Material and methods

A subset of the samples analyzed in Chapter 2 was chosen for the batch dissolution and disk carbonation experiments. Information on material characterization is listed in Table 3.1 and Table 3.2. Analytical details are described below. Eleven duplicates of the serpentine mineral abundance were examined using X-ray diffraction (XRD) to ensure the sampling was homogenous. The tailings samples were also analyzed three times before the average values were taken for their mineral abundance measurements (Table 3.2). Four types of acids were used to prepare the solvent solutions for the batch dissolution experiments including carbonic acid (H<sub>2</sub>CO<sub>3</sub>, compressed gas at 0.1 bar pCO<sub>2</sub>, Praxair), hydrochloric acid (HCl: A.C.S. Reagent Grade, Sigma-Aldrich Corporation), phosphoric acid (H<sub>3</sub>PO<sub>4</sub>: A.C.S. Reagent Grade, Sigma-Aldrich Corporation) and nitric acid (HNO<sub>3</sub>: Trace Metal Grade, Fisher Scientific International, Inc.). Concentrated acid was added to deionized water to obtain solutions of the desired pH. Carbonic acid (H<sub>2</sub>CO<sub>3</sub>) was introduced into the deionized water by constantly injecting compressed CO<sub>2</sub> gas at a flow rate of 200ml/min until the solution is at 0.1 bar pCO<sub>2</sub>. CO<sub>2(g)</sub> at 0.1 bar pCO<sub>2</sub> was used because the CO<sub>2</sub> concentration of power plant flue gas ranges from 5-20% (Prigiobbe et al., 2009; Songolzadeh et al., 2014). Disk carbonation experiments were performed using humidified CO<sub>2</sub> gas of the same concentration as the batch experiments. Details of the experimental setup and analytical procedures are described in the following sections.

Sample ID	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub> %	Fe <sub>2</sub> O <sub>3</sub> %	CaO %	MgO %	Na <sub>2</sub> O %	K2O %	
Brucite	3.49	0.41	0.93	1.97	59.28	0.07	0.01	
BrQtz mix	89.64	0.29	0.16	0.19	5.58	< 0.01	0.07	
Serpenti ne	38.80	0.58	7.46	0.35	37.84	0.05	0.12	
GK- PK21	38.74	3.57	7.46	7.24	28.77	0.59	1.29	
BD- FPCOM	34.26	0.16	9.625	0.02	41.92	0.065	<0.01	
Sample ID	Cr2O3 %	TiO <sub>2</sub> %	MnO %	P <sub>2</sub> O <sub>5</sub> %	SrO %	BaO %	LOI %	Total %
Brucite	< 0.01	0.01	0.04	0.05	< 0.01	0.01	33.30	99.55
BrQtz mix	< 0.01	0.02	0.01	0.01	< 0.01	< 0.01	3.82	99.78
Serpenti ne	0.24	0.04	0.10	0.02	< 0.01	0.01	13.38	98.97
GK- PK21	0.22	0.63	0.13	0.23	0.04	0.095	10.65	99.64
BD- FPCOM	0.55	< 0.01	0.11	0.002	< 0.01	< 0.01	12.9	99.61

 Table 3.1 Geochemical composition of experimented samples determined by x-ray fluorescence spectroscopy

Table 3.2 Table of sample characterization including results from XRD mineral abundance, TGA bruciteabundance, particle grain size, and BET reactive surface area.

Phase Abundance (wt%)	Natural Brucite Sample	Quartz Sample	Swift Creek Serpentinite	GK-PK21	<b>BD-FPCOM</b>
Serpentine (Lizardite)	4.20±0.12	-	90.29±4.8	43.00±2	77.00±3
Phlogopite	-	2.49	3.54±0.2	17.91	-
Clinochlore	-	-	-	12.32	-
Brucite	79.50±1.5	-	$1.76 \pm 1.6$	$1.50{\pm}1.4$	$10.50 \pm 2.5$
Diopside	-	-	-	3.31	-
Dolomite	6.26	-	-	0.96	-
Quartz	0.13	97.51	0.57	1.14	-
Spinel	-	-	-	1.66	6.40
Orthoclase	-	-	-	0.74	-
Albite	-	-	-	2.37	-
Andradite	-	-	-	8.51	-
Grossular	-	-	-	1.69	-
Enstatite	-	-	-	0.79	-
Magnesite	5.51	-	3.83	-	-
Pyroaurite	0.20	-	-	-	-
Forsterite	-	-	-	-	4.10
Hydromagnesite	5.46	-	-	-	-
Total	100.00	100.00	100.00	100.00	100.00
Grain size d(0.9) um	79	298	190	97	76
TGA (brucite wt%)	-	-	-	0.1	8.4
$A_{BET} (m^2 g^{-1})$	4.15	0.13	18.51	9.36	3.84

## **3.2.1** Batch dissolution

#### **3.2.1.1** Experimental methods

Slurries (~500ml) were prepared by adding 500mg of each pulverized sample to 500ml of acidic solutions. All batch dissolution experiments were conducted at a starting pH of 4.4. The solutions were prepared 24 hours before starting the experiments to ensure the full dissociation of the concentrated acids and equilibration with  $CO_2$  gas. For some experiments (serpentine),  $CO_2$  gas was not injected continuously into the solution. In others (brucite), CO<sub>2</sub> gas was injected continuously to avoid decarbonization of the fluid. Three reactors (500ml conical flasks) were used in each experimental run to compare the effects of agitation (shaking vs. stirring vs. still). Solid samples were added to the flasks followed by the solvent solution, after which the flasks were corked with rubber stoppers before being subjected to the designated agitation technique. The shaking agitation method was applied using a V.W.R. R Orbital Shaker Model 1000 at speed 4.5 (the lowest on the stir plate). The stirring agitation method was introduced using a 2 cm magnetic stir bar, and a Sorning R Stirring Plate set to 60 rpm (the slowest rotational speed available). A third reactor was left motionless on the lab bench to react without any form of agitation. The pH and solution chemistry of the slurry was measured at 15-minute, 30-minute, 2-hour, 4-hour, 6-hour and 8-hour intervals throughout the <72 hours duration. The pH of the slurry was monitored at the same time interval using a Thermal Orion 4-Star Plus Portable pH/I.S.E. meter with a measurable pH range between -2 to 19 and precision of  $\pm 0.002$ , as well as a Thermal Orion 9170BN 3-in-1 pH/automatic temperature compensation probe with a pH detection range from 0 to 14. Ten aliquots of ~5 mL slurry (total 50mls) were collected per reactor to ensure the impact of solvent depletion during dissolution is minimal. The reactors remained closed throughout the experiment except 74

during the sampling period. Solutions were at equilibrium with the atmospheric CO<sub>2</sub> at the beginning of the experiment. Slurry aliquots were analyzed for their dissolved Al, Ca, Fe, K, Mg, Na and Si. At the end of the batch dissolution experiments, the slurries were dispensed into 100ml Petri-dishes and dried at laboratory conditions prior to weighing and identification of the mineral phases from the post-experimental material. The experimental duration was controlled between 48-72 hours.

#### **3.2.1.2** Analytical procedures

Major oxide compositions of the initial samples were determined using X-ray fluorescence spectroscopy (XRF; Table 3.1) at A.L.S. Global Laboratories, North Vancouver, British Columbia, using lithium borate fusion digestion. Surface areas of the samples were determined via multipoint Brunauer–Emmett–Teller (B.E.T.) with  $N_2$  adsorption using the Quantachrome® Autosord-1 surface area analyzer and particle size distribution was determined using a Malvern® Mastersizer 2000 laser-diffraction particle size analyzer. Mineral abundance was characterized using powder Xray diffraction (XRD). Rietveld refinements, which are typically used to obtain quantitative information from XRD data, require that all mineral phases in samples to have defined crystal structure (Turvey et al., 2018a). For minerals such as serpentine, brucite and pyroaurite, whose crystal structure often exhibits preferred orientation problems (Wicks and Whittaker 1975), mineral abundance can be challenging to quantify. Preferred orientation occurs where platy or fibrous minerals preferentially align along with specific crystallographic directions. Preferred orientation often results in over- or under-reporting of mineral abundance using XRD (Turvey 2018). According to previous research, the relative errors on refined mineral abundance result from XRD tend to increase dramatically for phases present at <2wt% abundance (Raudsepp et al., 1999; Turvey et al., 2017, 2018; Wilson et al., 2006, 2009). Brucite, in particular, can be significantly

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underestimated, with relative errors as high as 250% (Turvey 2018). Relative error values are typically 90% when brucite present at 0.2-2wt% and are about 25% when brucite present at 10-15wt%; when serpentine and phlogopite is present 65-80 wt%, relative errors are ~6% (Hamilton et al., 2018; Turvey et al., 2018). Thus, the abundance of brucite, serpentine and phlogopite in the minerals and tailings samples were reported with relative uncertainty (Table 3.2).

At the end of each experiment, sample powders were retrieved and dried in lab air before being characterized using X-ray powder diffraction (XRD). Data were collected with a 0.03° 20 step size and a counting time of 7 s/step over a range of 3-80° 20. Search/match qualitative phase identification was completed with DIFFRACplus Eva 14 software (Bruker A.X.S., 2008) using the International Centre for Diffraction Data PDF-4+ 2010 database. Quantitative XRD analysis was not possible due to the small amount of sample available (<0.5g). Water samples were analyzed for Mg, Si, Ca, K, Al, and Na concentration using a Varian 725-ES inductively coupled plasma-optical emission spectrometer (ICP-OES) at the University of British Columbia. Standards were prepared by diluting concentrated QCS-27 ICP 27 multi-element Quality Control Standards to the concentration of 0.1 ppm, 0.5 ppm, 0.7 ppm, 1 ppm, 5 ppm, 10 ppm, 15 ppm, 20 ppm, and 30 ppm using 2% ultrapure nitric acid as blank and matrix. Uncertainties and standard deviation were obtained by analyzing 3-5 replicates of the prepared standards of known concentration during each analysis. Relative errors of each analytical run were calculated by formulating a linear relationship using 7 out of the 9 standards by their intensity, followed by computation of the known concentration of the other two standards. The relative error for each experiment run are summarized in Table 3.3. The detection limit of the analyzed major elements is reported in Table 3.4. It is worth noting that ICP-OES and other spectrochemical analyses are typically subject to error interferences (Krejčová et al., 2016; Morishige and Kimura 2008.; Sarojam 2010). Ionization interferences is a

phenomenon which shows a change in emission intensity, causing the ionization equilibrium to shift. Ionization interference is known to affect ICP-OES measurement when the coexisting elements are easily ionizable elements such as alkali metals. For easily ionizable elements such as Na, K, Rb and Cs, this generally results in higher intensity than the natural line (Morishige and Kimura 2008). For this reason, data quality assurance and quality control (QAQC) were performed on measured elemental concentration. Aluminum concentration in all experiments are below the detection limit of ICP-OES and are reported as half of the detection limit (0.05ppm, 1.86×10<sup>-6</sup> mol L<sup>-1</sup>). Based on sample characterization, the total [K<sup>+</sup>] in 500mg of serpentine is around  $2.55 \times 10^{-5}$ mol L<sup>-1</sup>, which is consistently lower than what was measured in solutions from most experiments (Figure 3.1). For comparative purposes, measured K content of solutions was compared with the total amount of K available for dissolution from mineral XRF analysis and the latter value is adopted. K measurements that were  $> 2.55 \times 10^{-5}$  mol L<sup>-1</sup> ([K<sup>+</sup>] based on XRF measurement) were not used and were replaced by  $2.55 \times 10^{-5}$  mol L<sup>-1</sup> (see Figure 3.1). The tables listing all the measured elemental concentration from each experiment can be found in Appendix C.4. Further data QAQC was performed by comparing experimental data with the corresponding charge balance models (refer to Appendix C.2 for details). In this study, the brucite dissolution rate was calculated based on solution Mg concentration, mineral reactive surface area, and flow rate following equation 1 (Eq.1: adapted from Daval et al., 2010)

$$R_{Mg} = \frac{\Delta_{[Mg]}}{\eta_{Mg} \,\Delta_t A_{BET}} \qquad \qquad \text{Eq. 1}$$

Where  $R_{Mg}$  is the reaction rate based on [Mg] (mol m<sup>-2</sup> s<sup>-1</sup>),  $\Delta_{[Mg]}$  is the change in [Mg] (mol),  $\eta_{Mg}$  is the mineral stoichiometric coefficient of Mg, and  $\Delta_t$  is the change in time (s). The dissolution


rates are expressed as the release of magnesium, and they are normalized to surface area (mol Mg  $m^{-2} s^{-1}$ ).

Figure 3.1 Measurement of cumulative  $[K^+]$  from all serpentine batch dissolution experiments compared with the total  $[K^+]$  in the serpentine sample (indicated by the green dashed line).

Table 3.3 Geochemical composition of experimented samples determined by x-ray fluorescence spectroscopy

Experiment Name	<b>Relative Error</b>
Brucite batch experiment	13.0%
Serpentine batch experiment	8.4%

Table 3.4 Elemental detection limit of different elements for the ICP-OES

Element	Al	Ca	Fe	К	Mg	Na	Si
Detection limit(ppm)	0.50	0.10	0.30	0.30	0.10	0.20	0.30

## **3.2.1.3** Geochemical calculations

Geochemical modelling and solution speciation calculations were performed using PHREEQC and the carbfix database (Parkhurst and Appelo 2013; Voigt et al., 2018). The carbfix database includes additional low-temperature Mg-silicate phases such as lizardite and sepiolite. Moreover, all solution speciation calculations were charge-balanced with respect to CO<sub>2</sub> content because experiments using HCl, HNO<sub>3</sub>, and H<sub>3</sub>PO<sub>4</sub> solutions were at equilibrium with lab air (~800ppm, 0.0008bar, -3.1pCO<sub>2</sub>) upon starting the experiments. Results from the solution speciation calculation was also performed on some literature data to make comparisons with results in the present study (Tosca and Masterson 2014; Tosca and Wright 2018; Tutolo and Tosca 2018). The saturation state of minerals was calculated utilizing this speciation model:

$$\Omega = \frac{Q}{K}$$
 Eq. 2

Where Q is the ion activity product, and K is the equilibrium constant or the mineral (i.e. Mg-silicate) solubility defined in the carbfix database. The relationship between [Mg<sup>2+</sup>] and pH during experiments that use different acid types fits a simple charge balance model given certain assumptions and equilibrium constraints. Minerals and tailings dissolution in an aqueous environment can be modelled as the release of Mg<sup>2+</sup> and OH<sup>-</sup> ions to balance H<sup>+</sup> in solution (Azizi and Larachi 2019). Charge balance models computed in PHREEQC were compared with results from all batch experiments for data quality assurance and quality control (QAQC) (details in

Appendix C and Appendix A). For brucite, only experiments that passed QAQC were analyzed further. For serpentine and tailings, experiments that did not pass the charge balance QAQC were also discussed and analyzed. A summary of the experimental conditions and duration of the batch dissolution are summarized in Table 3.5.

Table 3.5	Summary of experiment	tal conditions of all batcl	n dissolution (	experiments performed	at atmospheric
temperati	ure and pressure.				

Acid Type	Method	Sample	Duration (h)	Continuous supply of CO <sub>2(g)</sub>
H <sub>2</sub> CO <sub>3</sub>	Still, Stir, Shake	10%Brucite 90%Quartz	72.00	Yes
HNO <sub>3</sub>	Still, Stir, Shake	10%Brucite 90%Quartz	48.00	-
HCl	Still, Stir, Shake	10%Brucite 90%Quartz	48.00	-
H <sub>3</sub> PO <sub>4</sub>	Still, Stir, Shake	10%Brucite 90%Quartz	56.00	-
H <sub>2</sub> CO <sub>3</sub>	Still, Stir, Shake	Serpentine	72.00	No
HNO <sub>3</sub>	Still, Stir, Shake	Serpentine	48.00	-
HCl	Still, Stir, Shake	Serpentine	73.00	-
H <sub>3</sub> PO <sub>4</sub>	Still, Stir, Shake	Serpentine	48.00	-

#### **3.2.2** Disk carbonation

#### **3.2.2.1** Experiment method

The disk carbonation method was designed based on the existing microfluidic (Harrison et al., 2014) and column experiments for direct air capture of CO<sub>2</sub> via carbon mineralization (Harrison et al., 2013; Power et al., 2020). The experimental set up included a 60L polycarbonate reaction chamber with inlet and outlet ports for gas flow and two 4L interconnected conical flasks. During the experiment, the compressed CO<sub>2</sub> gas was continuously injected into the reaction chamber using Tygon R 3603 tubing at a rate of approximately 200ml min<sup>-1</sup>. During this process, CO<sub>2</sub> gas was humidified by flowing through two 4L interconnected conical flasks contains distilled water followed by a water bath at room temperature. CO<sub>2</sub> gas was humidified to reduce evaporative water loss from samples in the reaction chamber. Pulp samples of minerals and tailings were moulded into the shape of disks with a dimension of 17.9 mm radius and 1.8 mm thickness using a premade perspex glass mount and rod piston. The water to solid mass ratio is approximately 1:15, chosen to target 30% pore water saturation, value proposed in Harrison et al. (2015) to achieve maximum extent of reaction. Eight to twelve disks of each sample were premade and weighed for sampling and monitoring the change in chemical composition and weight through time. Sampling frequency was dependent on the experimental duration and varied from 48 hours to 96 hours. The experimental duration varied from ~165 hours to ~550 hours (23 days), depending on the mineralogy and the total amount of sample available. Temperature and humidity in the reaction chamber were monitored routinely using a portable HUMICAP® humidity and temperature probe HMP110 from VAISALA. The measurement range of the probe is from 0% to 100% relative humidity (R.H.) with the measurement accuracy of  $\pm 1.5\%$  R.H. The measurement range of the HMP110 temperature

probe is -40°C to 80°C with a precision of  $\pm 0.1$ °C. Temperature and humidity were stable throughout the experiment at around 22 $\pm$ 1°C and 95% $\pm 0.2$ %RH. The experimental conditions of the disk carbonation experiment and the initial carbon content of the samples are summarized in Table 3.6.

Experiment Number	Sample Name	Water/Solid Ratio	Duration(h)	Initial carbon content (%C)
1	10%Brucite90%Qtz	0.15	165	0.19
2	10%Brucite90%Qtz	0.15	354	0.19
3	10%Brucite90%Corudum	0.15	335	0.19
4	BD-FPCOM	0.15	526	0.041
4	GK-PK21	0.15	526	0.075
4	Serpentine	0.15	526	0.051
4	Forsterite	0.15	526	0.0037
4	BD-15FPD43	0.15	526	0.070
5	10%Brucite90%Qtz	0.075	334	0.19

Table 3.6 Summary of experimental conditions, sample names and initial carbon content.

## 3.2.2.2 Analytical method

Information on sample characterization is the same as what was reported for batch dissolution (Table 3.1, Table 3.2). Samples of pure forsterite and BD-15FPD43 were tested in addition to the samples used in batch dissolution. Forsterite grains were obtained from Ward's Natural Science (item #491,557). BD-15FPD43 is an exploration pulp sample from a drill core during a metallurgical test of the F.P.X. Nickel Property in central British Columbia, Canada. The mineral abundance of the forsterite and BD-15FPD43 determined using X-ray diffraction analysis is reported in Table 3.7.

Total inorganic carbon (T.I.C.) reported as %C (g of carbon/g of sample) of the disk samples were determined using a CM5130 acidification module with a Model CM5014 Carbon Dioxide Coulometer from U.I.C. Inc. Sample aliquots were acidified to release  $CO_2(g)$ , which was then quantified using a photodetector. The photodetector monitors the colour change of a colorimetric pH indicator. The detection range of the CO<sub>2</sub> coulometer ranges from <1 ug carbon up to 10,000 ugs of carbon for a single sample. Calcium carbonate standards were analyzed to calibrate the instrument before each analysis. The detection limit and uncertainty on measurements above this value are 0.02ug carbon  $\pm$  0.05. The carbon content of each sample measured before the experiment was subtracted from carbon content measured post-carbonation reaction to obtain the total carbon content gained from carbonation. Samples before and after the disk carbonation experiments were homogenized using a corundum mortar pestle before analyzed for total inorganic carbon (T.I.C.). Results from the disk carbonation experiments were compared with results from the flow-through presented in Chapter 2. The sample mass was monitored as an estimate of carbonation, but evaporative mass loss confounded the analysis; thus, the results were not reported or used for analysis.

 Table 3.7 Summary of XRD result for the sample characterization of forsterite and the BD-15FPD43 (Caroll et al., in prep)

Forsterite	wt%	BD-15FPD43	wt%
forsterite	94.9	serpentine	94.7
clinochlore	5.2	brucite	0.7
Total	100	forsterite	2.3
		diopside	2.3
		Total	100

## 3.3 Results

## **3.3.1** Batch dissolution experiments

Batch dissolution results of brucite and serpentine in HCl, HNO<sub>3</sub> H<sub>3</sub>PO<sub>4</sub> and solutions at 0.1 bar pCO<sub>2</sub> are summarized in Table 3.8. In these closed system experiments, Mg aqueous concentration is accumulative and would increase with time. The total Mg<sup>2+</sup> leached in solution represents the fast-reacting, loosely-bounded portion of Mg<sup>2+</sup> in the mineral structure because the experimental durations were less than 72 hours. Cumulative Mg<sup>2+</sup> released from mineral dissolution is measured from the aqueous solution (Table 3.8). The effect of agitation on mineral dissolution in a batch reactor is also examined by comparing the change in pH and cumulative [Mg<sup>2+</sup>]. In the brucite batch dissolution experiment, the dissolution and accumulation of Mg<sup>2+</sup> were continuous (Figure 3.2) compared to the decreasing  $[Mg^{2+}]$  in the serpentine experiment (Figure 3.3). Reaction rates of brucite in HCl, HNO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub> and the CO<sub>2</sub> solutions were compared with the corresponding rates measured in chapter 2 using the flow-through reactor (Figure 3.4). Potential mechanisms that explain the loss of  $[Mg^{2+}]$  in the serpentine experiments were discussed and examined further. Overall, experimental results were presented and discussed in two groups. Group 1 includes results from brucite batch dissolution; group 2 includes results from serpentine batch dissolution in which CO<sub>2</sub> content of the solution was not replenished with gas sparging.

Acid type	Agitation method	Sample name	Sample Mass (mg)	Post- experimental sample mass (mg)	wt% Mg dissolved in solutions	Vermiculite occurrence
$H_2CO_3$	Still	Brucite	500.0	480.0	44.0	
$H_2CO_3$	Stir	Brucite	500.0	475.1	89.0	
$H_2CO_3$	Shake	Brucite	500.0	453.8	93.0	
HNO <sub>3</sub>	Still	Brucite	500.0	495.0	11.2	
HNO₃	Stir	Brucite	500.0	488.4	12.0	
HNO₃	Shake	Brucite	500.0	494.8	11.0	
HCl	Still	Brucite	500.0	497.0	7.0	
HCl	Stir	Brucite	500.0	496.5	7.3	
HCl	Shake	Brucite	500.0	496.0	9.5	
${ m H_3PO_4}$	Still	Brucite	500.0	495.0	13.0	
${ m H_3PO_4}$	Stir	Brucite	500.0	495.0	14.3	
$H_3PO_4$	Shake	Brucite	500.0	495.0	11.4	
$\mathrm{H}_2\mathrm{CO}_3$	Still	Serpentine	499.0	483.9	4*	
$H_2CO_3$	Stir	Serpentine	500.0	468.8	20*	
$H_2CO_3$	Shake	Serpentine	500.0	481.0	15*	
HNO₃	Still	Serpentine	502.3	483.0	4*	Yes
HNO <sub>3</sub>	Stir	Serpentine	503.1	463.5	5*	Yes
HNO <sub>3</sub>	Shake	Serpentine	501.4	485.3	3*	
HCl	Still	Serpentine	501.7	501.7	2.2*	Yes
HCl	Stir	Serpentine	504.6	483.2	5*	
HCl	Shake	Serpentine	500.4	488.4	2.1*	Yes
${ m H}_3{ m PO}_4$	Still	Serpentine	503.1	490.0	1*	
${ m H_3PO_4}$	Stir	Serpentine	507.0	495.0	3*	
${ m H_3PO_4}$	Shake	Serpentine	508.5	494.0	3*	

Table 3.8 Summary of batch dissolution experimental results.

\*Cumulative  $[Mg^{2+}]$  taken from the first measured  $[Mg^{2+}]$  in solution due to the unexpected loss

of  $Mg^{2+}$  during the dissolution process.



Figure 3.2 Plots of solution pH (Row 1) and [Mg] mol L<sup>-1</sup> (Row 2) versus time of brucite batch dissolution in four acid types. The agitation effects are represented using plot symbols. Red indicates brucite dissolution in the CO<sub>2</sub> solution; green indicates dissolution in HNO<sub>3</sub>; black indicates dissolution in HCl, and blue indicates dissolution in H<sub>3</sub>PO<sub>4</sub>.



Figure 3.3 Plots of solution pH (Row 1) and [Mg] mol L<sup>-1</sup> (Row 2) versus time of serpentine batch dissolution in four acid types. The agitation effects are represented using plot symbols. Red indicates brucite dissolution in the CO<sub>2</sub> solution; green indicates dissolution in HNO<sub>3</sub>; black indicates dissolution in HCl, and blue indicates dissolution in H<sub>3</sub>PO<sub>4</sub>.



Figure 3.4 Plot reaction rate (mol Mg m<sup>-2</sup> s<sup>-1</sup>) versus time from brucite dissolution experiments using batch reactors and flow-through. Agitation effects were indicated using plot symbols; acid types were distinguished by colours.

#### **3.3.1.1** Brucite batch dissolution results

Magnesium concentration increased during brucite dissolution, and the dissolution rate was consistent with that measured using flow-through. In Figure 3.2, the change in [Mg<sup>2+</sup>] and pH is plotted with time for brucite dissolution in various acid types and agitation effects. For brucite dissolution in solution at 0.1 bar pCO<sub>2</sub>, CO<sub>2(g)</sub> was injected continuously into the solution, and  $[Mg^{2+}]$  increases progressively with time as more  $Mg^{2+}$  gets liberated from the brucite crystal structure. Solution pH and  $[Mg^{2+}]$  plateaued at ~9 and ~10×10<sup>-4</sup> mol L<sup>-1</sup> for brucite reaction in HCl, HNO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub> solutions after ~20 hours (Figure 3.2). In comparison, the peak [Mg<sup>2+</sup>] and pH for brucite reaction in solutions with elevated pCO<sub>2</sub> plateaued at ~6 and ~ $10 \times 10^{-3}$  mol L<sup>-1</sup> over the same time interval (Figure 3.2). Brucite dissolves faster in solution with elevated  $pCO_2$  and leached approximately 90% of the total Mg<sup>2+</sup> (Table 3.8). For brucite, experiments with agitation yield faster mineral dissolution and higher solution pH. Solution speciation calculation in PHREEQC demonstrates increasing brucite saturation index ( $\Omega_{bru}$ ) from <-10 to around -0.76 in experiments using HCl, HNO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub>, approaching brucite saturation (Figure 3.5). The change in [Mg<sup>2+</sup>] and pH followed the solution charge balance and showed comparable trends with the computed charge balance model (Appendix C, section C.2).

Brucite dissolution rates were calculated using Eq 1 and were compared with rates measured using the flow-through reactor (Figure 3.4). In Figure 3.4, brucite dissolution rates measured in the flow-through experiments are plotted as point symbols and are distinguished by colours for different acid types. Brucite dissolution was faster during the first 15 hours in HNO<sub>3</sub>, HCl and H<sub>3</sub>PO<sub>4</sub> before dropped to around 10<sup>-8</sup> mol Mg m<sup>-2</sup> s<sup>-1</sup> in both the flow-through and the batch dissolution experiments (Figure 3.4). For experiments in solutions with elevated pCO<sub>2</sub>, brucite reaction rates in the agitated reactors agree with the results from the flow-through. Brucite

dissolution in the CO<sub>2</sub> solution is higher than the rates in other acid types by more than one order of magnitude (Figure 3.4). Brucite dissolution kinetics is dependent on acid types, validates the flow-through results.



Figure 3.5 Plots of brucite ( $\Omega_{bru}$ ) saturation index versus time; experiments conducted in HCl, HNO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub> and the CO<sub>2</sub> solutions are differentiated by colours; the agitation effects are marked on the top right corner of each subplot.

## **3.3.1.2** Serpentine dissolution in batch reactors

#### **3.3.1.2.1** Fluid chemistry

In Figure 3.3, the change in  $[Mg^{2+}]$  and pH is plotted with time for serpentine dissolution in various acid types and agitation effects. Serpentine experiments that were agitated demonstrate higher solution pH and  $[Mg^{2+}]$  compared to those that were not. Solution pH and  $[Mg^{2+}]$  peaked at ~9 and ~5×10<sup>-4</sup> mol L<sup>-1</sup> for serpentine dissolution in HCl and HNO<sub>3</sub> (Figure 3.3). In comparison, the pH for serpentine dissolution in H<sub>3</sub>PO<sub>4</sub> and solution with elevated pCO<sub>2</sub> both plateaued at ~7. However, the  $[Mg^{2+}]$  in H<sub>3</sub>PO<sub>4</sub> is lower than that in the CO<sub>2</sub> solution by over one order of magnitude (Figure 3.3). Time-series measurements of solution chemistry illustrate the different timescale over which element sorption and leaching affect the concentration of various elements in solution (Figure 3.6, 3.7, 3.8). The concentration of Mg, Si, Fe and Al generally decreased with time in all experiments and, while Fe depletion in solution tends to show no relationship with either Mg or Si concentration, the magnitude of the total SiO<sub>2</sub> decrease generally correlates with the drop in Mg concentrations. Potassium and Ca accumulated in solution, and K enrichment tends to show correlations with the  $[Mg^{2+}]$  depletion (Figure 3.6, 3.7, 3.8). Serpentine dissolved the fastest in solution with elevated pCO<sub>2</sub> and leached the highest amount of Mg<sup>2+</sup> (Table 3.8).

Serpentine supersaturation prevailed after 5 hours of dissolution in HCl and HNO<sub>3</sub> (Figure 3.9). However, the saturation index of serpentine ( $\Omega_{serp}$ ) in the CO<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub> solutions ranges from -20 to -10, as shown in Figure 3.9, indicating that the solutions remained undersaturated with respect to serpentine. When plotting Mg concentration versus Si concentrations, all experiments-except for experiments in H<sub>3</sub>PO<sub>4</sub> demonstrates an Mg: Si ratio of ~6 (Figure 3.10, Figure 3.11). In all experiments, the slopes of the Mg versus Si graph do not correlate with the stochiometric Mg: Si ratio (1.45) of serpentine. Overall, the total amounts of Mg and Si depletion in solutions with

 $CO_2$  are higher than those in the other acids (Figure 3.6, 3.7, 3.8). Additionally, solution speciation calculations from PHREEQC using carbon content to charge balance show that HCl and HNO<sub>3</sub> solutions were supersaturated with respect to certain low-temperature, Al-free, Mg-silicate minerals (i.e. saponite, sepiolite) (Figure 3.12). Results from the speciation calculation also demonstrate that the partial pressure of  $CO_2$  was at  $10^{-3.1-3.5}$  bar before dropped to  $10^{-4.5}$ , following [Mg<sup>2+</sup>] depression (Figure 3.12). Serpentine rates of reaction in batch reactors were not computed because [Mg<sup>2+</sup>] dropped over time.



Figure 3.6 Concentration of Mg, Si, Al, Ca, Fe and K in solution over time for Serpentine dissolution in four acid types with shake agitation.



Figure 3.7 Concentration of Mg, Si, Al, Ca, Fe and K in solution over time for serpentine dissolution in four acid types with stir agitation.



Figure 3.8 Concentration of Mg, Si, Al, Ca, Fe and K in solution over time for serpentine dissolution in four acid types without agitation.



Figure 3.9 Plots of serpentine ( $\Omega_{bru}$ ) saturation index versus time; experiments conducted in HCl, HNO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub> and the CO<sub>2</sub> solutions are differentiated by colours; the agitation effects are marked on the top right corner of each subplot.



Figure 3.10 Concentrations of Mg plotted versus concentrations of Si for serpentine batch dissolution in HCl, HNO<sub>3</sub>. The dashed red lines indicate a slope of 2/3, which is representative of the Mg:Si molar ratio of sepiolite and serpentine.



Figure 3.11 Concentrations of Mg plotted versus concentrations of Si for serpentine batch dissolution in H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>CO<sub>3</sub>. The dashed red line indicates a slope of 2/3, which is representative of the Mg/Si molar ratio of sepiolite and serpentine.



Figure 3.12 Plots of pCO<sub>2</sub>, saponite saturation index and sepiolite saturation index versus time; experiments conducted in HCl, HNO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub> and solutions at 0.1 bar pCO<sub>2</sub> are differentiated by color; the agitation effects are distinguished using plot symbols.

# 3.3.1.2.2 X-ray diffraction results

Lizardite dominates the XRD patterns of solids recovered from the serpentine batch experiments. The positions of these peaks are generally consistent from sample to sample located at 24° 20, 44° 20 and 72° 20 (Figure 3.13). A secondary alteration product is identified in the XRD pattern of post-experimental solids (see Figure 3.13 and Appendix C section C.3 for details). The positions of the peaks are generally consistent from sample to sample and are indicative of low angle basal reflections at 7° 20 (Figure 3.13), which we identify as vermiculite. The detection of vermiculite, however, is not consistent from sample to sample. Post-experimental products from dissolutions in HNO<sub>3</sub> and HCl both demonstrate the formation of vermiculite, while those in CO<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub> do not. Previous studies have documented that vermiculite often forms via secondary alteration of biotite or phlogopite (Kuwahara and Aoki 1995; Wiewióra and Dubińska 1987). Ten quantitative XRD results showed that there is ~3.45wt% phlogopite in the initial serpentine sample (Table 3.1), meaning that vermiculite formation could be associated with phlogopite alteration. Except for vermiculite, no other secondary phases are noted from the XRD pattern of the postexperimental products.



Figure 3.13 X-ray powder diffraction patterns of serpentine reaction products after batch dissolution in HNO<sub>3</sub> with the agitation of stir and shake. Vermiculite peaks located at around 7° 2θ positions.

## **3.3.2** Disk carbonation experiments

Disk carbonation experiments differed from all other experiments in that the labile Mg in each sample was converted to solid Mg-carbonate material. This experiment tests whether or not measured labile Mg contents can be carbonated under ambient lab conditions. The results of all disk carbonation experiments are summarized in Table 3.9. The table includes information on sample name, total inorganic carbon content gained, and total inorganic carbon estimated based on labile Mg content and XRD mineral abundance. Brucite was studied in experiments 1, 2, 3 and 5 with different variables in experimental conditions. Experiment 4, on the other hand, involved samples of serpentine, olivine and three tailings. The extent of carbonation is measured in terms of the total inorganic carbon content (T.I.C.) expressed as grams of carbon per grams of sample (%C). T.I.C. before the disk carbonation experiments is subtracted from the T.I.C. after the experiment to evaluate the change in carbon content with time. Brucite gained the most amount of total carbon in experiment 2, followed by experiments 1 and 5 (Table 3.9). The increase in carbon content for the serpentine is minimal but is slightly higher than that of forsterite. BD-FPCOM has a higher brucite abundance than GK-PK21 and 15FPD43 and, therefore, gained more carbon through the carbonation process (Table 3.9). T.I.C. estimated based on XRD abundance of brucite, serpentine, and forsterite in each sample is also reported in Table 3.9. These values represent the maximum carbon content that is attainable in each sample if all labile Mg is converted to solid carbonate material. The stoichiometry that converts Mg to C is 0.8, assuming the formation of hydromagnesite [Mg5(CO3)4(OH)2·4H2O].

Experiment Number	Sample Name	T.I.C. gained (Cf-Ci)	T.I.C. estimate based on XRD brucite content	T.I.C. estimate based on XRD serpentine content	T.I.C. estimate based on XRD forsterite content
1	10%Brucite90 %Qtz	0.426	1.421	-	-
2	10%Brucite90 %Qtz	0.558	1.421	-	-
3	10%Brucite90 %Corundum	0.283	1.421	-	-
4	<b>BD-FPCOM</b>	1.410	1.648	0.313	0.007
4	GK-PK21	0.281	0.185	0.221	-
4	Serpentine	0.049	-	-	0.395
4	Forsterite	0.006	-	-	0.130
4	15FPD43	0.276	0.148	0.394	0.003
5	10%Brucite90 %Qtz	0.165	1.421	-	-

Table 3.9 Summary of disk carbonation experimental results.

### **3.3.2.1** Disk carbonation results

The measured carbon content in brucite (Figure 3.14), serpentine, forsterite (Figure 3.15) and tailings (Figure 3.16) is compared with the estimated maximum carbon content calculated by converting all labile Mg to solid Mg-carbonates. The estimated maximum carbon content is calculated by assuming all labile Mg measured in the flow-through is carbonated, and hydromagnesite  $[Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O]$  is formed with the stoichiometry of C/Mg = 0.8. For mineral samples, the value of estimated carbon content converted from all labile Mg in brucite is 1.42 (Figure 3.14), and that of serpentine and forsterite (Figure 3.15) are 0.41 and 0.15, respectively. For tailings, quantitative XRD mineral abundance was also included for the calculation. BD-FPCOM has the highest brucite content and, therefore, the highest labile Mg content (1.12×10<sup>-3</sup> mol) compared to that of the other two tailings samples. Based on XRD mineral abundance results,  $\sim 9.17 \times 10^{-4}$  mol of labile Mg is from brucite dissolution, and  $\sim 2.05 \times 10^{-4}$  mol labile Mg is leached from serpentine. Converting the total labile Mg to total carbon content yields the estimated maximum carbon content in BD-FPCOM, which is ~2.14, as shown in Figure 3.16. Similarly, the maximum carbon content estimated for GK-PK21 and BD-15FPD43 are 0.34 and 0.55, plotted as dashed black and red lines in Figure 3.16.

Time-series measurements of carbon content increased in brucite (Figure 3.14) and tailings (Figure 3.16) while that of serpentine and forsterite (Figure 3.15) remained low and steady throughout the experiment. The extent of carbonation achieved in brucite is consistently lower than the estimated value in all experiments. For brucite, the highest carbon content gained among the four experiments was 0.558, which can only account for ~40% of the estimated maximum carbon content. In contrast, the carbon content gained in BD-FPCOM, BD-15FPD43 and GK-PK21 after the experiment is much closer to the estimated value. The maximum carbon content

estimated varied for different tailings due to the differences in their mineral abundances. BD-FPCOM has the highest brucite content, thus has the highest estimated carbon content, followed by BD-15FPD43 and GK-PK21. For GK-PK21, the carbon content gained during the experiment was the closest to the estimated value. Serpentine and forsterite carbon content before and after the disk carbonation experiment fluctuate around their initial values, showing neither noticeable increase nor decrease. The total carbon content gained in both samples ranged from 0 to  $\sim$ 0.001, demonstrating a limited extent of carbonation.



Figure 3.14 Plot of carbon content (g carbon/g sample) with time (h) for brucite disk carbonation experiments. The estimated maximum carbon content is plotted as a dashed blue line.



Figure 3.15 Plot of carbon content (g carbon/g sample) with time (h) for forsterite and serpentine disk carbonation experiments. The estimated maximum carbon content is plotted as a dashed red (serpentine) and green(forsterite) line.



Figure 3.16 Plot of carbon content (g carbon/g sample) with time (h) for tailings disk carbonation experiments. Estimated maximum carbon content is plotted as a dashed blue (BD-FPCOM), red (BD-15FPD43) and black (GK-PK21) line.

The results from the disk carbonation experiments are compared with the estimated maximum carbon content in a bar graph, as shown in Figure 3.17. In general, the extent of carbonation achieved in the disk carbonation experiment is lower than that characterized using flow-through dissolution. Because the labile Mg in mineral samples of serpentine and forsterite was not well-characterized using the disk carbonation experiment, the carbon content gained in the tailings seems to be primarily contributed by brucite carbonation (Figure 3.15). The labile Mg content measured in the tailings samples using flow-through is divided based on their XRD mineral abundance of brucite and serpentine. The uncertainties that associate with quantifying brucite abundance of low values is quite significant. Error bars are plotted on the disk carbonation results to account for the relative errors from quantitative XRD measurements of brucite. The value of relative errors adopted for tailings with <2wt% brucite and >10wt% brucite are 90.8% and 25.0%. XRD brucite abundance in BD-FPCOM; thus, ranges from 8.8wt% to 14wt%, corresponds to the carbon content in solid to range from 1.31 to 2.19. Similarly, samples of BD-15FPD43 have 1.33wt% to 0.064wt% brucite, meaning that the corresponding carbon content attainable through brucite carbonation can be as high as 0.22. Brucite and serpentine abundance of GK-PK21 is 1.5  $\pm$  1.4wt% and 43  $\pm$  2wt%, meaning that the attainable carbon content can range from 0.02 to 0.49. The variation in brucite abundance shows that serpentine in tailings was not carbonated even though the disk carbonation measurements seem to fall in the serpentine carbonation range (Figure 3.17). Overall, the carbon content gained in tailings is much higher than pure mineral phases, and labile Mg from brucite is the main contributor to the carbonation reaction. What remains unresolved is the ability of disk carbonation experiments to access the labile Mg content of high brucite content samples such as brucite mineral samples. Factors that are attributing could be the transport of CO<sub>2(g)</sub> within the disk with extremely high brucite content, which, because it is not

realized in mine tailings samples, is not expected to be a limitation for the application of the disk carbonation test.



Figure 3.17 Carbon content (g carbon/g sample) (%C) gained in each sample based on flow-through results compared with results from disk carbonation, assuming the formation of hydromagnesite. Carbon content gained through brucite reaction (red), and serpentine reaction (grey) are indicated separately for tailings samples. The results from the disk carbonation are plotted as a dashed line for comparison.

## 3.4 Discussion

#### **3.4.1** Batch dissolution

Batch and flow-through experiments are conventional experimental techniques that have been used to generate kinetic data to determine rates of mineral dissolution (Daval et al. 2013; Gleisner and Herbert 2002; Martinez et al., 2014; Metz and Ganor 2001; Stillings and Brantley 1995). One of the essential differences between batch and flow-through experiments is that the solution chemistry in the batch experiment is cumulative. Because batch dissolution experiments are intended to replace flow-through dissolution for characterizing labile Mg of minerals and tailings in the present study, the following discussion focus on quantifying the cumulative Mg content.

Shaking and stirring are common agitation effects used to assist dissolution experiments in batch reactors (e.g. Cama et al., 2000; Ganor et al., 1995; Nagy et al., 1991; Nagy and Lasaga 1992). Serpentine dissolution in stirred and shaken flasks showed consistently higher Mg<sup>2+</sup> release and elevated pH buffering (Figure 3.3). In contrast, the effect of agitations on brucite dissolution is not as evident (Figure 3.2). A possible explanation for this observation is that brucite has a smaller reactive surface area (4.15 m<sup>2</sup> g<sup>-1</sup>) compare to serpentine (18.51 m<sup>2</sup> g<sup>-1</sup>). Serpentine is a layered Mg-silicate mineral with a sizeable reactive area, meaning that it can be affected by the spalling and abrasion effect of a stirred reactor more than Mg-hydroxide mineral brucite. The increase of mineral surface area during stirred batch and flow-through dissolution experiments are commonly observed and documented in published studies (Amrhein and Suarez 1992; Cama et al., 2000; Cama and Ganor 2006; Malmström and Banwart 1997; Nagy and Lasaga 1993; Soler et al., 2008; Stillings and Brantley 1995; White and Brantley 1995). Furthermore, the effect of shaking can be characterized as a liquid-solid mass transfer process that allows the exchange of soluble ions between solution and suspended particles (van Grinsven and

van Riemsdijk 1992; Rhodes and Gaden 1957). Results from the present study show that stirring and shaking do impose accelerating effects on the dissolution of silicate minerals. Reactors that were agitated can trigger more  $Mg^{2+}$  leaching from minerals and tailings than those that were not. Nevertheless, the purpose of this study is to use batch reactors to quantify leachable  $Mg^{2+}$  instead of determining dissolution kinetics of minerals and tailings. Data was not collected to assess whether the dissolution rate is faster in experiments with or without agitations and whether the reactions are transport-controlled or reaction-controlled. Thus, the rest of the discussion will focus on quantifying labile Mg content in brucite and serpentine using batch dissolution.

## 3.4.1.1 Assessing labile Mg of brucite using batch reactors

Based on experimental results of brucite and serpentine, batch dissolution techniques seem to be more successful for quantifying the reactivity of Mg-hydroxides compare to Mg-silicates. In general, the  $[Mg^{2+}]$  increases with time in all brucite batch experiments, and that the cumulative  $[Mg^{2+}]$  in the CO<sub>2</sub> solution is higher than that in HCl, HNO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub> by over one order of magnitude, as shown in Figure 3.2. Brucite dissolution in HCl, HNO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub> seems to be proton-activated during which  $Mg^{2+}$  detachment from the brucite mineral surface consumes H<sup>+</sup> (Pokrovsky and Schott 2004). Increasing  $[Mg^{2+}]$  leads to the consumption of  $[H^+]$  and higher solution pH, exposing brucite particles under a more alkaline environment with less H<sup>+</sup> activity. In contrast, the solution charge balance during brucite dissolution in CO<sub>2</sub> includes protonated inorganic ligands such as HCO<sub>3</sub><sup>-</sup> which results in less H<sup>+</sup> consumption and higher solution buffering. The neutral to acidic conditions allows the CO<sub>2</sub> solution to remain far away from brucite saturation, allowing brucite to dissolve continuously at far-from-equilibrium conditions and promote the release of Mg<sup>2+</sup> (Figure 3.5).

Total cumulative  $[Mg^{2+}]$  from brucite batch dissolution is compared with that from the flow-through. As shown in Figure 3.18, the fraction of  $Mg^{2+}$  reacted in the batch reactor is consistently lower by ~10% compared to that in the flow-through experiments. Such observations can be attributed to two main reasons. First, the reaction time in the batch reactors is shorter than that in the flow-through (~72 hours versus ~100 hours). This is because the batch dissolution experiment is designed to replace flow-through dissolution as a fast and inexpensive method to assess labile Mg. Therefore, the experimental duration is reduced from >100 hours to <72 hours. Second, the dissolution process of the flow-through reactors involves passing the fresh acidic inlet solution through a packed bed of mineral grains versus in the batch reactor, the pH of the reacting

solutions increased as more  $Mg^{2+}$  released. Interpreting rate data from the results of flow-through and batch dissolution shows good agreement (Figure 3.4), such that with longer reaction time, the labile Mg measured using flow-through dissolution will agree with that measured using batch dissolution. Therefore, batch dissolution can be an easy and inexpensive alternative to flowthrough dissolution for quantifying the labile Mg of Mg-hydroxides.



Figure 3.18 Fraction of Mg<sup>2+</sup> reacted from brucite dissolution in solutions at 0.1 bar pCO<sub>2</sub>, HCl, HNO<sub>3</sub>, and H<sub>3</sub>PO<sub>4</sub>. Red column shows results from brucite dissolution in flow-through reactors; black line with diamonds indicate cumulative [Mg<sup>2+</sup>] results from batch reactors.
### 3.4.1.2 Assessing labile Mg of serpentine using batch reactors

For mineral dissolution studies in a batch reactor, one of the main disadvantages is that solution chemistry varies with time and may cause minerals other than the investigated phase to precipitate (Arthur et al., 2000). Solution parameters such as pH, alkalinity, elemental (i.e. Al, Mg, Ca) concentration change simultaneously and complicate interpretations of the experimental data. Precipitation of secondary phases is a particularly severe problem at neutral to alkaline pH, where the solution commonly supersaturates with respect to certain mineral phases (Bales and Morgan 1985; Nagy et al., 1990). In these cases, the experimental results cannot be used to quantify reactivity for mineral carbonation.

Experimental results retrieved from serpentine dissolution in batch reactors were unexpected and were studied extensively to understand the factors that lead to the drop in  $[Mg^{2+}]$ . Typical trends from the serpentine dissolution data reveal that the decreasing concentration of Mg, Si, Al, Fe is accompanied by the increasing concentration of Ca and K (Figure 3.6, 3.7, 3.8). Additionally, the drop in Mg and Si concentration is much higher than that of Al and Fe. The average Mg:Si ratio in the solution is ~6 (Figure 3.10, Figure 3.11), and that serpentine becomes oversaturated in HCl and HNO<sub>3</sub> solutions (Figure 3.9). The dependence of serpentine labile Mg on acid types is evident given that the solutions with CO<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub> remained neutral to acidic pH, and  $[Mg^{2+}]$  in the CO<sub>2</sub> solution is the highest. However, the decrease in  $[Mg^{2+}]$  remained problematic, and three possibilities were proposed and discussed further to explain such phenomenon:

- 1) phlogopite alteration to vermiculite;
- 2) formation of low-temperature Mg-Si phases (saponite, sepiolite or serpentine) and
- 3) readsorption of  $Mg^{2+}$  back to the serpentine via surface-exchange processes.

Qualitative XRD results of the post-experimental solids from serpentine batch dissolution in HNO<sub>3</sub> and HCl indicate the appearance of a secondary mineral phase vermiculite (Figure 3.13). Phlogopite alteration to vermiculite at room temperature has been investigated experimentally by many earlier studies (Boettcher 1966; Hoda and Hood 1972; Kuwahara and Aoki 1995; Malmström and Banwart 1997; Toksoy-Köksal et al., 2001; Wiewióra and Dubińska 1987; Wilson 1966). Kuwahara and Aoki (1995) mentioned that phlogopite alteration typically consumes  $Mg^{2+}$ and produces K<sup>+</sup>, which is consistent with the elemental trends observed in the serpentine experiments (Figure 3.6, 3.7, 3.8). The replacement of interlayer K<sup>+</sup> with hydrated cation  $Mg^{2+}$ during phlogopite leaching can be described using the following chemical reaction (Hoda and Hood 1972) during which 2 moles of K<sup>+</sup> is consumed for every 1 mole of  $Mg^{2+}$ :

$$\frac{1}{2}$$
 Mg<sup>2+</sup> + K-phlogopite = Mg-vermiculite + K<sup>+</sup> Eq. 3

Further evidence supporting this transformation reaction is performed by analyzing the source of K<sup>+</sup> in the sample. XRD mineral abundance analysis shows that there are ~3.45wt% phlogopite present initially in the serpentine, representing  $4.22 \times 10^{-5}$  mol of K in 0.5g of the sample. The XRD measurement of K in serpentine is higher than that of the XRF measurement, demonstrating that the phlogopite is potentially the only source of K in the serpentine sample (Table 3.10). The increasing [K<sup>+</sup>] suggests that phlogopite dissolution and alteration is in parallel with the serpentine reaction in acidic solutions. The decrease in [Mg<sup>2+</sup>] can, therefore, be explained via the formation of vermiculite. However, if assuming two moles of K<sup>+</sup> was released to consume one mole of Mg<sup>2+</sup> and all the K<sup>+</sup> in the sample were released, the amount of vermiculite formed can only account for less than 1ppm of Mg<sup>2+</sup> loss in solution as shown in Figure 3.19. The total consumption of Mg<sup>2+</sup> from each experiment are plotted as columns, and the calculated Mg<sup>2+</sup> consumption via K<sup>+</sup> production are plotted as dotted lines (Figure 3.19). In summary, phlogopite

alteration to vermiculite can explain  $[K^+]$  increase during serpentine dissolution. However, the concentration of K in solution is not enough to explain the total consumption of  $[Mg^{2+}]$ .



Figure 3.19 Plots of total [Mg<sup>2+</sup>] loss during serpentine batch dissolution in CO<sub>2</sub>, HCl, HNO<sub>3</sub>, and H<sub>3</sub>PO<sub>4</sub> solutions compare to calculated [Mg<sup>2+</sup>] consumed via vermiculite precipitation.

 Table 3.10 Table comparing the [K] in a sample based on phlogopite abundance and the XRF geochemical composition.

		moles of K based on XRD abundance	moles of K based on XRF K2O content
Sample Weight (g) XRF K <sub>2</sub> O content % Phlogopite XRD abundance wt%	0.5 0.12 3 54+0 2	4.22E-05	1.27E-05

In addition to Mg, concentrations of Si, Al and Fe also showed definite trends of decreasing abundance, which may suggest the formation of potential low-temperature Mg-silicates (Figure 3.6, 3.7, 3.8). Many Mg-rich phyllosilicate minerals can precipitate directly from surface water under atmospheric conditions (Tosca and Masterson 2014). Given that the average Al concentration measured in experimental solutions ranges from 0 mol L<sup>-1</sup> to  $\sim 10^{-6}$  mol L<sup>-1</sup>, Mgsilicate phases that can form are anticipated to be either Al-low or Al-free. Mg-silicate minerals such as Sepiolite [Mg<sub>8</sub>Si<sub>12</sub>O<sub>30</sub>(OH)<sub>4</sub>(O.H.)<sub>2</sub>•8H<sub>2</sub>O]; Kerolite [Mg<sub>3</sub>Si<sub>4</sub>O<sub>10</sub>(O.H.)<sub>2</sub>H<sub>2</sub>O] and Saponite [Ca<sub>0.1</sub>Na<sub>0.1</sub>Mg<sub>2.25</sub>Fe<sup>2+</sup>0.75Si<sub>3</sub>AlO<sub>10</sub>(O.H.)<sub>2</sub>•4(H<sub>2</sub>O)] are typically Al-free, low-temperature Mgsilicates. Because of their unusual chemical composition and structure, Mg-silicates formation in water is rapid and poorly crystalline, which explains why they can be undetectable by XRD. Three earlier experimental studies have demonstrated that high pH, soluble Mg<sup>2+</sup>, and Al-free systems favour the production of Mg-silicate minerals such as stevensite, kerolite, talc and sepiolite at room temperature (Table 3.11). In these studies, mineral precipitation experiments were conducted to precipitate these low-temperature Mg-silicate minerals, and their experimental conditions are compared with this study. As shown in Table 3.11, the experimental duration of these mineral precipitation experiments ranges from 4 weeks to 7 months, which is much longer compared to that in this study. Although two of the three studies observed visible precipitates formed within the first 48 hours of the experiments (Tosca et al., 2011; Tutolo and Tosca 2018), the Mg and Si concentrations in their studies were much higher than that in this study. More importantly, Zeyen et al. (2019) concluded that Fe-bearing kerolite or smectite phases are more evident when [H4SiO4] is above 0.4mM. Tosca and Masterson (2014) also demonstrated low-temperature Mg-silicates precipitation in solutions with high Mg:Si ratio (i.e. Mg:Si=6) and Mg, Si concentration ( $\sim 10^{-3}$  M). The Mg:Si ratio in most of the serpentine experiments conducted in this study is ~6, which is

comparable with conditions in experiments performed by Tosca and Masterson (2014). However, the average [Si<sup>4+</sup>] in solutions of this study is ~  $10^{-5}$  mol L<sup>-1</sup>, which is lower than the threshold [Si<sup>4+</sup>] found in Zenyen et al. (2019). Furthermore, the present study has no direct evidence of Mgsilicate mineral precipitation, which suggests that [Si<sup>4+</sup>] concentration is the fundamental control for low-temperature Mg-silicate formation. PHREEQC speciation calculation showed that only HCl and HNO<sub>3</sub> solutions were supersaturated with respect to sepiolite and saponite (Figure 3.12). However, the value of saturation indexes ( $\Omega$ ) computed for solutions from this study is ~ ten times lower than that computed for experiments conducted by Tutolo and Tosca (2018) (Figure 3.20). Additionally, in Figure 3.21, solubility lines of crystalline talc (Jones, 1986), sepiolite, and kerolite (Stoessell, 1988) are plotted in a solubility diagram showing the log  $(a(Mg^{2+})/a(H^{+})^{2})$  versus log (a(SiO<sub>2</sub>)) of the solutions. Both the CO<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub> solutions are located below the solubility lines of crystalline talc, and only HNO<sub>3</sub> and HCl solutions are located between the solubility line of talc and sepiolite, which is consistent with values of the saturation indexes computed using PHREEQC (Figure 3.12). Thus, it is unlikely that precipitation of low-temperature Mg-silicates is causing Mg<sup>2+</sup> depression because all solutions from the serpentine batch dissolutions are below the solubility line of these minerals (Figure 3.21).

It is also noted that serpentine reprecipitation is not occurring because the dissolution and precipitation kinetics of serpentine is very slow under atmospheric conditions (Bach et al., 2006; Klein et al., 2013; Moody 1976; Roy and Roy 1954). Even though both the HCl and HNO<sub>3</sub> solution were supersaturated with respect to serpentine (Figure 3,11), the rate of Mg, Si, Al and Fe consumption in HCl and HNO<sub>3</sub> solutions ranged from 10<sup>-9</sup>-10<sup>-12</sup> mol s<sup>-1</sup>, which is comparable with the rate of serpentine recrystallization at 280°C (Lamadrid et al., 2017) versus the 25°C used in this study. Serpentinization at room temperature within 72 hours, thus, is not a suitable hypothesis

to explain the trends observed in the serpentine experiments. Al-free, low-temperature Mg-silicates formation is also not favoured under the experimental conditions in this study. Therefore, the precipitation of secondary low-temperature Mg-silicate phases is not contributing to the loss of  $Mg^{2+}$  in the serpentine batch dissolution.

	Experiment duration	Temperature	рН	Mg [mol/l]	Si [mol/l]	Mg-Si phase precipitated
Tosca et al, 2013	4 weeks to 7 months	25±0.1°C	8.7, 9.0, 9.4	1.0E-02 - 5.02E-03	1.07E-02 - 7.61E-03	stevensite, kerolite, talc, sepiolite
Tutolo and Tosca 2018	94 days	21±0.1°C	10.2	1.0E-02 - 5.02E-03	2.3E-03 - 6.4E-03	sepiolite, stevensite, talc
Tosca et al., 2011	4 weeks to 7 months	25±0.1°C	6-9	1.0E-02 - 5.02E-03	2.3E-03 - 6.4E-03	kerolite, talc
This study	48-72 hours	25±0.1°C	4-8	1.32E-04 - 4.82E-04	5.27E-05 - 1.01E-04	-

Table 3.11 Summary of experimental conditions and conclusions from three literature studies



Figure 3.20 Plots of lizardite, sepiolite and CO<sub>2</sub> saturation index versus time (days). The CO<sub>2</sub> saturation index is computed and examined to make a comparison with this study. Data adapted from Experiments B, C, F and H from Tutolo and Tosca., 2018. Solution speciation calculations are performed using PHREEQC (Tutolo and Tosca., 2018).



Figure 3.21 Solubility diagram showing apparent solubilities of different Mg-silicates phases in solutions. Solubility lines of crystalline talc (Jones, 1986), kerolite and sepiolite (Stoessell, 1988), amorphous sepiolite from Wollast et al. (1986) are presented in dashed line. Plot symbols stand for water solutions samples from serpentine batch dissolution experiments.

The remaining hypothesis addressing the issue of  $[Mg^{2+}]$  depression is the exchange of cations between mineral surfaces and solution. Each hydroxide ion on the surface of serpentine particles is assumed to be a possible adsorption site for protons and other cations or anions (Bales and Morgan 1985). At constant pH, dissolution, adsorption controls the development of surface charge. The removal of a given number of surface hydroxide Mg<sup>2+</sup> would result in the creation of an equal number of silica surface sites (Bales and Morgan 1985; Thom et al., 2013). On average, the ratio of molar Mg to Si release should be higher during the incongruent stage versus the 1.4-1.5 during the congruent stage. During a pH shift from 4.4 to 8, hydrogen-ion concentration typically changes by 1000-fold due to the exchange between protons and Mg<sup>2+</sup> at the serpentine surface, and such processes may be reversible. In the pH-jump experiment performed by Thom et al. (2013), serpentine dissolution kinetics indicated that steady-state dissolution is independent of dissolution history. The effect of rapid change in bulk water chemistry (i.e. dissolution history) is significant for steady-state serpentine dissolution. As shown in this study, the switch from pH 4.4 to 8 when adding 0.5g of serpentine to 500 ml solution acts like a pH-jump experiment that suddenly changes the chemical environment of serpentine dissolution from acidic to alkaline. During this time, silica release shows a weaker pH dependence and becomes more dominant. The solubility of CO<sub>2</sub> also increased, which drives the dissolution of CO<sub>2</sub> in a sealed flask. Since no external sources of CO<sub>2</sub> are available, the pCO<sub>2</sub> in solution decreased with the increase in CO<sub>2</sub> solubility (Figure 3.12). More importantly, the depression of  $Mg^{2+}$  means less  $HCO_3^{-}$  is needed for solution charge balance, which therefore drives decarbonization of the fluid. Finally, in order to restore the original dynamic equilibrium of the Mg:Si ratio at the mineral surface, readsorptions of  $Mg^{2+}$  back to the mineral surface could have occurred and acted as a sink for  $Mg^{2+}$ .

The fraction of  $Mg^{2+}$  at the surface of the serpentine grains is estimated based on the method adopted by Daval et al. (2013). The number of "surface" Mg atoms corresponds to the sum of the total amount of Mg atoms in the outermost (001) face (brucite-like sheets) and the four lateral faces of the crystallite (i.e., (100),  $(\bar{1}00)$ ,  $(0\bar{1}0)$ , (010) planes) (detail information in Appendix B, section B.2). By combining information on the unit cell parameters of lizardite, B.E.T. surface area and sample mass, the fraction of  $Mg^{2+}$  at the serpentine surface accounts for ~6.42% of the total  $Mg^{2+}$ , which corresponds to ~14ppm of  $[Mg^{2+}]$  in solution. Similarly, the fraction of  $Si^{4+}$  at the serpentine surface is ~5.6%, which is ~10ppm. As shown by the calculation, no experiments have leached total [Mg<sup>2+</sup>] >14ppm suggesting that the dissolution of serpentine is incongruent and remains at the mineral surface. Based on the observations from this study and what was shown in the pH-jump experiment from Thom et al. (2013), it seems that there is a dynamic equilibrium for Mg<sup>2+</sup> and Si<sup>4+</sup> amount at the serpentine surface for a given pH. Serpentine dissolution is independent of the dissolution history. A switch from acidic to alkaline could result in readsorptions of Mg<sup>2+</sup>, while a jump from alkaline to acidic condition would drive a new stage of preferential release of Mg<sup>2+</sup> over Si<sup>4+</sup>. Thus, in the serpentine batch dissolution experiments, depression of [Mg<sup>2+</sup>] could be due to the establishment of a new Mg:Si dynamic equilibrium at the mineral surface as the pH moves from acidic to alkaline. Nonetheless, further experimental and analytical studies on serpentine dissolution may be required to validate this hypothesis. The trends observed and analytical approaches that were taken in this study enable more in-depth observations into the serpentine dissolution pathways and their dependence on pH. Batch dissolution can not replace flow-through for quantifying the labile Mg of Mg-silicates because Mg<sup>2+</sup> is lost during the dissolution process and cannot be measured.

Overall, the assessment of serpentine reactivity in batch reactors is not successful due to the continuous drop in  $[Mg^{2+}]$  observed in most experiments. The reduction of Mg concentration complicates the interpretation of the experimental data. A geochemical calculation was conducted in PHREQQC, calculating the lowest Mg and Si concentration required at alkaline pH before approaching serpentine supersaturation (Table 3.12). The model suggests that if the experiment reduces the solid to liquid ratio to a value that prevents serpentine supersaturation, the measured Mg concentration may approach the detection limit of ICP-OES (Table 3.12). This means we will have to switch analytical techniques with more precision (i.e. ICP-MS), which is not a feasible resolution to characterize ultramafic tailings' reactivity at low expense. Moreover, batch dissolution experiments that fail to account for precipitation of secondary phases or allow the reactions to occur for a sufficient period time are inadequate for retrieval of meaningful data. This means the measured  $[Mg^{2+}]$  is not be representative of the labile Mg content of serpentine or tailings. Thus, the current batch dissolution protocol is not an ideal alternative of the flow-through dissolution for accessing minerals and tailings reactivity for mineral carbonation.

 Table 3.12 PHREEQC modelled results of sample mass required for serpentine batch dissolution in 500ml
 solution to reaching supersaturation.

Acid Types	рН	[Mg] ppm	[Si] ppm	Serpentine SI	[Mg] mol/l	[Si] mol/l	Serpentine Sample mass (g)
0.1 bar CO <sub>2</sub>	8.06	41.51	3.00	0.1	1.71E-03	1.07E-05	0.16
HNO <sub>3</sub> /HCl	9.06	0.62	1.50	0.19	2.55E-05	5.34E-06	0.0024
H <sub>3</sub> PO <sub>4</sub>	9.01	1.08	1.00	0.26	4.44E-05	3.56E-06	0.0041

### 3.4.2 Disk carbonation discussion

#### **3.4.2.1** Disk carbonation for assessing labile Mg of minerals

Labile Mg content is converted to solid Mg-carbonate mineral as a measure of reactivity during disk carbonation experiments. Mineral carbonation reactions occurred in porous media, where the pores are only partially water-filled, often involves three steps, 1) diffusion of CO<sub>2</sub> into pore water between mineral grains, 2) dissolution of Mg-hydroxide and Mg-silicate minerals, releasing labile Mg<sup>2+</sup> into pore spaces and 3) saturation and precipitation of amorphous Mg-carbonate and hydrated Mg carbonate minerals such as nesquehonite [MgCO<sub>3</sub>·3H<sub>2</sub>O], hydromagnesite [Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(O.H.)<sub>2</sub>·4H<sub>2</sub>O] (Harrison et al., 2015; Harrison 2014). These processes have been documented and observed in bench-scale column experiments and natural weathering of tailings in many previous studies (Assima et al., 2012, 2014a, 2014b; Bea et al., 2012; Harrison et al., 2015, 2016; Harrison et al., 2013; Hövelmann et al., 2012; I. Power et al., 2014). The dissolution environment of the disk carbonation experiment is significantly different from that in the flow-through and batch dissolution experiments because the reactions did not proceed in an aqueous environment.

Results from the disk-carbonation experiment of brucite demonstrate that the labile Mg content of brucite is less than that determined using flow-through and batch dissolution. During the four experimental runs of brucite, different changes were made to increase the extent of carbonation (Figure 3.14). In experiment 2, the experimental duration was increased by ~200 hours compared to that in experiment 1. In experiment 3, the mineral mixture of brucite and quartz was switched from quartz to corundum. Moreover, in experiment 5, the initial water content of the brucite sample was reduced by 50%, leaving brucite reacting with relatively dry pore space. As a result, longer experimental duration seems to have contributed to a greater carbonation extent, and

experiments conducted using low water content do not promote brucite dissolution and carbonation. This is consistent with the results from Assima et al., 2013 for carbonation of chrysotile mine residues, which showed restricted reaction progress with low water content. Overall, brucite only carbonated 10-15% of its labile Mg<sup>2+</sup> in the three different experimental runs (Figure 3.14). This implies longer reaction time, and enough water is required to enhance the reactivity of brucite. The mass of water loss is observed in all experiments, which could be attributed to both evaporation and the incorporation of water into hydrated carbonate phases (Harrison et al., 2015). Another possible control that limits the brucite dissolution-carbonation reaction may be surface passivation. Surface passivation often results from the initial rapid dissolution at the brucite mineral surface, which further leads to the formation of Mg-carbonate mineral, fills the pore spaces around the grains, prevents further reaction into the core of the mineral (Harrison et al., 2015). Nevertheless, further experimental and analytical work (such as S.E.M., etc.) on the carbonated disk samples could resolve such hypotheses and maximize the access of labile Mg in brucite for mineral carbonation. However, this work is beyond the scope of this thesis and is not discussed here.

The results of the serpentine and forsterite minerals demonstrate that disk carbonation cannot be used to assess labile Mg content of minerals with relatively slow reaction kinetics. Based on results from chapter 2, the reaction rate of serpentine is 100 times slower than brucite, even for the labile fraction, which explains the ~0 carbon content increase in serpentine and forsterite after the 3-4 weeks disk carbonation experiment (Figure 3.15). Future experiments that are >100 times longer will be needed for labile Mg in the serpentine and forsterite to carbonate, which is not desirable considering the purpose of this study is to assess labile Mg using a quick and easy experimental method.

#### **3.4.2.2** Disk carbonation for assessing labile Mg of tailings

Based on the results presented in Figure 3.17, the abundance of brucite seems to be the primary control of tailings' reactivity during disk carbonation experiments. Among the three tailings samples, BF-FPCOM has the highest brucite content, which leads to the highest increase in the carbon content (Figure 3.16). Both BD-15FPD43 and GK-PK21 demonstrate complete carbonation of their labile Mg in brucite (Figure 3.17). Brucite dissolution-carbonation reaction seems to be the main driver for the increase in carbon content in the tailings sample, while serpentine illustrates limited to no extent of carbonation. The fast dissolution of brucite can create more pH buffering within the pore fluid, which subsequently promotes CO<sub>2</sub> dissolution and Mgcarbonate precipitation. Disk carbonation of the tailings sample also suggests that longer reaction time is required for the labile fraction within serpentine to be accessed. The slow-reacting nature of silicates makes them less than ideal for providing carbonation reactivity during the disk carbonation experiment. The readily accessible Mg<sup>2+</sup> within tailings is mostly sourced from brucite rather than serpentine, which is supported by the observation on the serpentine dissolution rate documented in Chapter 2. Assessment of the labile Mg in serpentine requires reaction time to be 100 times longer than the present duration, which is not feasible.

To conclude, disk carbonation experiments suggest brucite is the primary source of labile Mg during disk carbonation experiments. Additional factors that could affect carbonation reactions in porous media are water content and experimental duration. Chemical environments and tailings' mineralogy still play significant roles in determining tailings' reactivity for mineral carbonation. Nevertheless, higher-resolution estimation of the carbon sequestration reactivity would also depend on: sources of  $CO_{2(g)}$ , physical properties of tailings, chemical environment as well as the

reaction time scale. Disk carbonation is not a quick and easy alternative to the flow-through dissolution for accessing the carbon sequestration capacity of tailings. For a lab-scale assessment, disk carbonation requires a long reaction time, which is not desirable for the purpose of this study.

### 3.5 Summary

Proper characterization of the CO<sub>2</sub> sequestration potential of mine wastes provides meaningful insight into the implementation of their CO<sub>2</sub> capture and storage techniques. When performing the flow-through dissolution experiments (described in Chapter 2), we encountered technical difficulties and financial concerns that drive the motivation to design new experimental protocols for assessing reactivity. Here, we have proposed the use of batch dissolution and disk carbonation experiments to perform quick and low-cost tests for examining the labile Mg content of minerals and tailings. The <72 hours batch dissolution experiment measures labile Mg but changes solution chemistry as materials dissolve. Magnesium concentration during brucite batch dissolution was cumulative and comparable with that measured using flow-through, which demonstrates that the current batch dissolution protocol can assess the labile Mg content of Mghydroxides. Serpentine dissolution in batch reactors resulted in [Mg<sup>2+</sup>] depression meaning the labile Mg content cannot be assessed. The potential cause of [Mg<sup>2+</sup>] decrease is surface cationexchange at the serpentine surface, which subsequently decreases alkalinity due to the solution charge balance. In this case, increase the liquid to solid proportion will not resolve the issue of decreasing [Mg<sup>2+</sup>], meaning that the current batch dissolution protocol is not a feasible way of performing the reactivity measurement for Mg-silicates and tailings. Further experimental and analytical work could elucidate the mechanisms that drive  $[Mg^{2+}]$  decrease in batch reactors.

Finally, experimental results from disk carbonation have important implications because the experiment models coupled mineral dissolution-carbonation reaction in porous media, assessing labile Mg through detecting the total carbon content in the sample. Important conclusions that are drawn from the disk carbonation include (1) brucite disk-carbonation was not complete during the 3-4 week experiment, and the supply and transport of  $CO_{2(g)}$  could be limiting; (2) integrating results from chapter 2, the dissolution kinetics of serpentine is 100 times slower than brucite, meaning that Mg-silicates take much longer time to dissolve and carbonate during the disk carbonation. Assessing labile Mg in serpentine or other Mg-silicates would imply increasing the experimental duration by >100 times, which is also not feasible for attempting to measure labile Mg content quickly. Nevertheless, disk carbonation provides insights into controls of coupled mineral dissolution-carbonation reaction in pore space, including brucite content, pore saturation and reaction kinetics. These findings will contribute to the discovery of more refined strategies to quantify labile Mg content and characterize the capacity of mine tailings for carbon capture and storage.

# **Chapter 4: Conclusions**

#### 4.1 Dissertation objectives and outcomes

Extensive evidence on the anthropogenic cause of climate change can be obtained from the comprehensive IPCC report published in 2007 (Hellevang 2015; IPCC 2007, 2018). As the threat of global warming and climate change increases continuously, CO<sub>2</sub> emissions into the atmosphere should be reduced considerably. Carbon mineralization sequesters CO<sub>2</sub> by combining CO<sub>2</sub> with metals to form carbonate minerals. A range of natural rock formations and industrial wastes are appropriate feedstock for carbon mineralization owning to their high abundance of alkaline earth metal-bearing minerals (Power et al., 2013). Mines that generate ultramafic and mafic mine wastes (e.g. tailings) are one of the valuable feedstocks for carbon mineralization and the focus of this study. The main advantages of carbon mineralization using ultramafic mine tailings are that they can sequester more than their greenhouse gas emission to create environmental benefits that utilizing waste products. More importantly, ultramafic mines generate vast quantities of mine tailings that offer a readily available, fine-grained feedstock for carbonation (Wilson et al., 2014). Carbon mineralization reactions in mine tailings are favoured at atmospheric conditions, and the carbonation processes can be readily controlled and manipulated (Power et al., 2013). In this study, the reactivity and capacity of ultramafic mine tailings to sequester  $\mathrm{CO}_{2(g)}$  produced from mine truck operation and electricity generation are highlighted together with the fundamentals of mineral carbonation and evaluation of its applicability to the mining industry as a method to mediate climate change. Accurate estimation of tailings' reactivity further determines the capacity of which ultramafic mines to sequester CO<sub>2</sub> over the mine life. Appropriate testing protocols and methods allow correct assessment of tailings' reactivity and explore tailings' properties that contribute to high carbon sequestration potential. Given the relatively sluggish kinetics of dissolution under the ambient conditions and mild acidity present in many tailings facilities, targeted dissolution of the readily extractable, labile cations present in highly reactive phases and on mineral surfaces should be prioritized over the dissolution of recalcitrant cations present within the core of relatively unreactive silicate phases. Brucite  $[Mg(OH)_2]$  represents a highly reactive phase that is common but minor in ultramafic mine tailings. In contrast, serpentine  $[Mg_3Si_2O_5(OH)_4]$  represents a less reactive phase but with high carbon sequestration potential due to its high abundance.

The primary objectives of this thesis were to 1) elucidate the controlling reaction mechanisms during Mg-hydroxide and Mg-silicate mineral dissolution in order to use labile cations and more specifically labile Mg to define reactivity, 2) examine the variabilities of labile Mg with respect to the mineralogy and chemical conditions (acid types, pH) and 3) develop alternative experimental and analytical protocols for fast, easy and economic viable assessments of reactivity for carbon sequestration. The outcomes of this work are listed in response to the three objectives.

For studies on reactivity, we found that: 1) carbon mineralization reactivity of tailings can be defined by quantities of labile Mg that are sourced via fast bulk dissolution of the trace Mghydroxides and the transient surface-reaction of Mg-silicates; 2) the definition of labile Mg is  $Mg^{2+}$ reacting faster than ~10<sup>-8</sup> mol Mg g<sup>-1</sup> s<sup>-1</sup> as this is the average steady-state dissolution rate of pure brucite at pH=3-5; this rate scales with the fraction of reacting labile Mg.

For examining labile Mg variabilities, we identified that: 1) labile Mg content is dependent on both the mineralogy and the surrounding geochemical environment of tailings; 2)  $CO_2$  promote the dissolution of serpentine the same way as it enhances the dissolution of brucite, serpentine reactivity increase with the partial pressure of  $CO_2$  in solution and 3) the mineral composition of

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tailings and the source of  $CO_{2(g)}$  is the ultimate control on labile Mg content when applying this assessment in the field.

Finally, for assessing and measuring labile Mg, we established that: 1) the flow-through time-resolved analysis (FT-TRA) method (De Baere et al., 2013) employed in the present study shows promise for future use in the assessment of mine tailings reactivity. Its advantages span experimental design and analytical capabilities; 2) the <72 hours batch dissolution experiments with agitations can correctly assess the reactivity of brucite, but cannot assess the labile Mg content of serpentine. Serpentine dissolution during the transient stage models a reversible surfaceexchange process that can lead to the depression of Mg<sup>2+</sup>. Although adjusting the liquid to solid ratio may prevent solution from oversaturated with serpentine and other low-temperature Mgsilicate phases, it will not resolve the issue of Mg<sup>2+</sup> depression and accurately assess the labile Mg content of serpentine; 3) disk carbonation experiment offers opportunities to simulating minerwater-gas interaction during mineral carbonation, measures labile Mg content by converting to solid Mg-carbonate mineral. Disk carbonation experiments validated the results from chapter 2, demonstrating Mg-hydroxides reacts orders of magnitude faster than Mg-silicates. Longer experimental duration is needed to assess the labile Mg content in Mg-silicate phases meaning that this is not an ideal method for a quick reactivity measurement. The fundamental limiting factors that contribute to the coupled mineral dissolution-carbonation reactions in porous media include the supply of  $CO_{2(g)}$  and water content.

In conclusion, this study provides new pathways and insight into characterizing reactivity of ultramafic mine tailings for carbon sequestration via mineral carbonation. Labile Mg and its availability is not merely a case of steady-state dissolution of highly reactive minerals. It is a much more complex concept, and we have worked on the development of more detailed and more direct estimates of characterizing and measuring reactivity. The reaction conditions adopted in three experimental techniques are representative of the earth's surface and atmospheric conditions. The results of this thesis propose ideas for measuring and utilize mineral dissolution rates for quantifying the capacity of ultramafic mine sites to sequester  $CO_2$ . More importantly, the research makes meaningful contributions to the development of experimental techniques that could benefit future research in evaluating  $CO_2$  sequestration potential in ultramafic mine tailings.

#### 4.2 Definition and controls of labile Mg for carbon sequestration

The experimental works conducted for this study provide essential insights into how to assess and potentially improve the efficiency to sequester CO<sub>2</sub> through mineral dissolution reactions, particularly within ultramafic mine tailings. The most significant conclusion from all the experimental studies presented in this thesis is the definition of labile Mg. Labile Mg is more applicable for minerals and tailings in ultramafic mines because they are more abundant with Mg cations. Labile Mg refers to Mg<sup>2+</sup>, which is loosely bounded, fast reacting and rapidly leached under atmospheric conditions. Our definition of labile Mg depends on two things, 1) the minimum dissolution rate that is considered to be 'rapid' and 2) the fraction of Mg in a rock or mineral that can be leached at or above this rapid rate. Labile Mg is not merely Mg<sup>2+</sup> leached under transient conditions. We define labile Mg to be Mg<sup>2+</sup> that can react faster than  $\sim 10^{-8}$  mol Mg g<sup>-1</sup> s<sup>-1</sup> as this is the steady-state dissolution rate of pure brucite between pH=3 and pH=5. The quantity of labile Mg scales with the rate of labile Mg because the rate is dependent on the mass of reacting solid. We understand that drawing this delineation between labile and non-labile Mg is somewhat arbitrary; however, it is necessary if we aim to explore the capacity and applicability of tailings to sequester CO<sub>2</sub> to mitigate climate change. We observe that quantity of labile Mg in minerals and tailings changes with mineralogy and chemical environment (pH, acid types). For tailings, the maximum labile Mg can be obtained from the abundance of their Mg-hydroxides and Mg-silicates, assuming reaction in solution at 1bar pCO<sub>2</sub>. This number will be refined and reduced when accounting for the surrounding dissolution environment (acid type, pH, pCO<sub>2</sub>), which will determine the labile Mg content (i.e. reactivity). Labile Mg opens a new pathway towards our understanding of the natural weathering of minerals as part of the earth's geochemical process. We used experimental methods that are conventional for determining the mineral dissolution kinetics

to characterize innovative concepts for carbon mineralization. Labile Mg avoids the underestimation of ultramafic tailings capacity for mineral carbonation. More importantly, carbon sequestration using mine tailings opens up the opportunity for future ultramafic mining to be carbon-neutral and potential carbon negative.

#### 4.3 Development of analytical techniques for assessing reactivity

Results from all three experimental approaches are integrated, and valuable conclusions are drawn here. The disk carbonation experiments confirm that mineral dissolution rate exerts an essential control during the carbonation process. Flow-through and batch dissolution experimental results both reveal that brucite dissolves orders of magnitude faster than serpentine, even for the labile portion. Thus, minerals that are carbonated first during the ~500-hour disk carbonation experiment is brucite. The increase in total carbon content in the tailings sample can be attributed to brucite carbonation. The labile portion of serpentine will not be reactive unless the reaction proceeds approximately 100 times longer. Therefore, results from disk carbonation, flow-through and batch dissolution all agreed between each other regarding the dissolution kinetics of Mg-hydroxides, Mg-silicates and their contribution to the labile Mg content in tailings.

The measured dissolution rate of brucite using the batch reactor and the flow-through are comparable while that of serpentine is not due to the unexpected loss of  $Mg^{2+}$ . As oppose to flow-through, the solution chemistry in the batch reactor is cumulative and variable. Phlogopite alteration to vermiculite and serpentine surface-exchange reaction are the potential causes of  $Mg^{2+}$  depletion. Although the assessments of serpentine labile Mg content were unsuccessful, it can be concluded that having a stable supply  $CO_{2(g)}$  can potentially limit the extent of  $Mg^{2+}$  drop because the solution can sustain sufficient alkalinity. More importantly, the analytical approaches that were taken to investigate the issue of  $Mg^{2+}$  depression enable an in-depth understanding of serpentine dissolution during the transient stage and its' dependence on pH. Further experimental and analytical approaches should be taken to investigate the sink of  $Mg^{2+}$  during serpentine batch dissolution.

The experimental methods adopted in this study are all conventional methods for measuring mineral dissolution rates (batch, single-pass flow and column experiments), but they were all substantially modified. The results from the flow-through dissolution study validate the FT-TRA module as a meaningful and versatile experimental technique to characterize labile Mg. We have identified several advantages for its application in assessing the reactivity of tailings. The advantages are (1) high temporal resolution resulting from the small volume of the reactor and time-resolved pH and solution chemistry analysis; (2) faster attainment of steady-state mineral dissolution kinetics, which stems from the small reactor volumes and short residence time of eluent in the reactor (De Baere et al., 2015); (3) short experiment duration (<120 hours) enables quick assessments of the labile cations through mineral dissolution; 4) inexpensive analytical technique needed which brings cost-benefit. As for limitations, the FT-TRA often experiences difficulties when studying samples of small (<53um) grain size and high clay content. Clay-rich tailings and ultrafine particles often result in significant clogging within the flow-through reactor, which then led to leaks of the effluent solution and the failure of the experiment. Moreover, the inline pH meters used in the FT-TRA are not designed for long-term continuous usage. They often result in instrumental drifts, which makes the module labour-intensive since back-up measurements need to be taken continuously. Overall, the FT-TRA module presented here is, by far, the most useful tool for assessing labile Mg in minerals and tailings. With measurements of both the rate and quantities of Mg<sup>2+</sup> leached, labile Mg is defined and used for characterizing reactivity for mineral carbonation.

In contrast, the batch dissolution protocol developed in this study is not as successful. Based on the experimental result, the current experimental protocol is only suitable for studying mineral dissolution and quantifying labile Mg of the monomineralic Mg-hydroxides. Samples with high brucite content showed positive results in batch dissolution with continuous  $CO_{2(g)}$  flow, which suggests that having a stable source of  $CO_{2(g)}$  can prevent  $[Mg^{2+}]$  decrease. Mg-silicates are predominantly abundant in ultramafic tailings meaning that the batch dissolution protocol adopted in this study needs to either omitted or substantially redesigned to replace the FT-TRA for characterizing labile Mg. Geochemical modelling of the experimental condition suggests that increasing the solid to liquid ratio can prevent the formation of secondary phases. However, this is not a feasible way to prevent the loss of labile Mg during the experiment because surfaceexchange reaction at the serpentine surface is potentially the major sink of  $Mg^{2+}$ .

The disk carbonation experiment developed in this study is a new method with advantages and potentials. The disk carbonation experiments conducted in this study successfully verified results from the flow-through and suggest that labile Mg in brucite is the most accessible Mg<sup>2+</sup> during industrial-scale, short-term mineral carbonation. The advantages of the approach are (1) the quick and easy experimental setup; (2) not labour-intensive and do not need constant monitoring; (3) cost-effective analytical technique that directly measures the extent of carbonation. Nevertheless, this approach cannot quickly and successfully measure the labile Mg content of Mgsilicates due to their sluggish dissolution kinetics. It will be more applicable for estimating longterm mineral carbonation capacity of tailings if we leave samples to react for months. Overall, disk carbonation is a vital progression for the design of these testing protocols since it allows coupled dissolution-precipitation reactions.

To conclude, based on results from the geochemical modelling and three experimental studies presented in this thesis, the FT-TRA is currently the most suitable and matured testing protocol for measuring labile Mg and estimating the carbon sequestration capacity of minerals and tailings. The proposed batch dissolution and disk carbonation protocols can be two starting points

for the future advancements of new experimental approaches. New analytical and experimental techniques can build upon what was encountered in all three experiments and address these potential problems in order to design a quick, cost-friendly and easy method to assess reactivity (labile Mg) in minerals and tailings for carbon mineralization.

### 4.4 Suggestions for future research

Prospective works to further advance the current experimental work for carbon mineralization are proposed from four perspectives, including (1) use FT-TRA to determine labile Mg values for other ultramafic minerals and apply the concept of labile Mg to other labile cations, Ca, Fe, K, Na, for different rocks; (2) investigate how Mg<sup>2+</sup> depression in a batch reactor is related to the serpentine surface-exchange process; (3) advance the existing experimental protocols and come up with new ideas for experimental design.

Given the success of using FT-TRA for measuring labile Mg content of brucite, serpentine and tailings, other ultramafic minerals and tailings should also be examined. Labile Mg content of minerals such as pyroxene, olivine, amphibole and tailings from nickel-copper, platinum group metals, chromium and asbestos mines can also be assessed using flow-through dissolution experiments. This serves to build a database for the development of potential testing protocols or a computational geochemical model. The model is expected to have the capability to provide information on labile Mg content and dissolution kinetics of various minerals and ultramafic tailings, with the input information, including but not limited to, mineral composition, pH and CO<sub>2</sub> concentration. A computable numerical model like this would require a large amount of experimental data and technological support. The success of a digitalized testing protocol or numerical model will revolutionize the research in carbon sequestration using mine tailings and will enable strong application capability. Moreover, the knowledge of defining labile Mg for assessing reactivity of ultramafic mine tailings is applicable to other industrial waste feedstocks such as steel-slags. Steel slag is waste in the steel industry, and it releases both Ca<sup>2+</sup> and Mg<sup>2+</sup> upon dissolution, which generates enormous potentials for sequestering CO<sub>2</sub>. In this case, both

labile Ca and labile Mg can be used to define reactivity and help with accurate estimations of the CO<sub>2</sub> sequestration capacity.

To further examine the issue of decreasing  $[Mg^{2+}]$  in a batch reactor, additional experiments and analyses are required. Batch experiments involving pH-jump from acidic to alkaline will help validate the hypothesis of serpentine surface-exchange during dissolution. Similar to what was conducted in Thom et al., 2013, if we can demonstrate that surficial Mg<sup>2+</sup> dissolution is reversible after pH jump from acidic to alkaline, we can confirm that the depression of Mg<sup>2+</sup>is caused by the surface-reaction of serpentine. More importantly, this would imply that there is a dynamic equilibrium between Mg<sup>2+</sup> and Si<sup>4+</sup> at the serpentine surface during incongruent dissolution. Batch dissolution experiment with pH-jump would also provide new insight into the dissolution pathway of labile Mg in serpentine. Furthermore, analytical electron microscopic (AEM) on the post-experimental product of serpentine should be conducted using transmission electron microscopy (TEM) or scanning electron microscope (SEM) to observe any structural modification and secondary phase formation. Because the scale of both mineralogical and chemical heterogeneity may be beyond the resolution of conventional analytical tools (SEM), TEM is proposed here for such studies (e.g. Buseck 1980; Veblen and Ferry 1983). TEM can examine reaction topology in great detail; for example, Yau et al., 1984 has described TEM observations of phlogopite altering to vermiculite in samples after the dissolution experiments. The textural relations between the serpentine layers can be observed on the scale of a few tens of angstroms, providing new insights into the reaction mechanism involved in the dissolution processes and imply the existence of pathways for fluid flow and ion transport. TEM analysis can also demonstrate whether the dissolution model of serpentine starts from the basal surface or the

edge. Physical models from the TEM will also justify the source of labile Mg from serpentine, deliver implications for other sheet silicates and provide more convincing evidence for this study.

An extension to the current discussion on factors that contribute to Mg<sup>2+</sup> depression in the batch reactor includes the formation of silica-gel and increasing element solubility. According to results from previous research, the dissolution of sheet silicates commonly results in the aggregation of gel-like particles with the increase of time (Carroll-Webb and Walther 1988; Lin and Clemency 1981). Such a process would often affect the interpretation of surface-controlled reaction because diffusion through the aggregate could play a role. Moreover, earlier mineral dissolution studies often found the solubility of Al, Fe and Mg in solution during mineral dissolution to be a concern, especially when dissolving clay minerals (Carroll-Webb and Walther 1988). The use of an Al-complexing agent at near-neutral pH to prevent precipitation or adsorption of Al, Fe and Mg on clays to prevent such issues have been documented (Carroll-Webb and Walther 1988). Clemency and Lin (1981) also presented the used ion-exchange resins to control solution composition (Al, Mg, K and pH) during the dissolution of illite and phlogopite. These two hypotheses were not directly discussed in the chapters due to the lack of analytical data and experimental evidence. However, they should be considered and noted for future experimental studies on clay mineral dissolution kinetics and may lead to the success of using batch dissolution techniques to measure labile Mg of tailings and Mg-silicates.

To prevent problems such as clogging, leaking, elemental concentration depression encountered during serpentine and tailings dissolution using the flow-through and batch dissolution, a combination of the two experimental techniques may be considered (Carroll-Webb and Walther 1988). For example, mixed-flow batch reactors or continuous stirred tank reactors (CSTR) that allow fluids to have a short residence time, maintain solution pH while solving the problems of leaking or clogging because the reactor is slightly bigger and can prevent internal pressure build-up. Both reactors are configured much like a batch reactor, except reactants and products continuously flow in and out of the reactor (Chapman et al., 2017; Danish and Rashid 2015; Posey-Dowty et al., 1986). Steady-state flow-through reactors are ideal for industrial purposes when large quantities of material are to be processed. The stirring can also effectively enhance the dissolution of tailings and minerals by producing ultrafine particles. The output composition should be identical to the composition of the solution inside the reactor, and the dissolution rate is a function of residence time and rate of reaction (Carroll and Knauss 2005; Chapman et al., 2017; Lejre et al., 2019; Pokrovsky et al., 2005). The detailed experimental design will have to be considered in detail and can be very different from the conventional CSTR used in chemical engineering (Danish et al., 2015; Méndez-Acosta et al., 2010). However, both methods have high potentials of becoming very useful for the later experimental work studying labile cations and assessing the carbon mineralization reactivity.

Lastly, a new assessment protocol, inspired by the current disk carbonation experiment set up, is also proposed here for future research. The experimental set up includes the use of the current reaction chamber and a bundle of tailings samples that can be placed on top of a series of small CO<sub>2</sub> injection tubes. Experiments can be conducted by injection of CO<sub>2</sub> gas of various concentration through the tubes, into the tailings over a fixed experimental period (ranges from hours to months). The extent of mineral carbonation can be monitored as a function of time with the collection of samples throughout the experiment and perform total inorganic carbon analysis. This experimental protocol is very similar to disk carbonation except that it allows the coupled reaction of mineral dissolution and precipitation to occur in environments that are comparable with tailings. This experimental method does not necessarily solve the slow reaction kinetics of Mgsilicates, and the experimental duration of this protocol is expected to be very long. The experimental design aims to mimic the industrial-scale implementation of mineral carbonation technology in a lab environment to ensure the success of such technology in the field. Regardless of whether the protocol will work as expected, the present study has inspired the discovery of more refined strategies to quantify labile Mg and characterizing the capacity of mine tailings for capturing and storing CO<sub>2</sub>.

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## Appendix A Data quality control protocol

A set of data quality assurance and quality control (QAQC) protocol is applied to all the dissolution experiments conducted in this thesis. Data from both the flow-through and batch dissolution experiment presented in this thesis were tested and verified using this protocol to ensure the quality of each experiment. Only data that pass the QAQC protocol are used for the subsequent analysis and interpretation. The QAQC protocol involves three tests: comparing manual pH measurements and automated inline pH measurements (applicable to flow-through experiments only), fitting data to a charge balance model, and mass balance calculation that compares cumulative  $[Mg^{2+}]$  in solution with sample mass loss due to leached  $Mg^{2+}$ .

All three tests are used to validate data from the flow-through dissolution experiment. Two QAQC tests are performed on data from the batch dissolution experiment since no automatic inline pH measurements are available. During the flow-through dissolution experiment, aqueous  $Mg^{2+}$  leached create buffering capacity for the effluent pH. Such buffering capacity will progressively decrease as fewer  $Mg^{2+}$  are leached. The effluent pH, thus, converges with the eluent pH indicate zero or no release of  $Mg^{2+}$ . Manually measured effluent pH using the portable pH meter is calibrated daily during the experiment. Plots of pH vs Time(h) of all flow-through dissolution experiments can be found in Appendix B.2. Measurements disagreement within ±0.02 pH unit are considered negligible, and data are used for further analysis. Detailed results of chapter 2 on charge balance model fitting can be found in Appendix B.2, and mass balance calculations can be also be found in tables listed in Appendix B.2. Detailed results of chapter 3 charge balance can be found in Appendix B.2.

#### A.1 Mass balance calculation

Mass balance calculations involve comparing aqueous  $[Mg^{2+}]$  and total  $Mg^{2+}$  consumed from the solid sample. For pure mineral samples, cumulative  $[Mg^{2+}]$  from the flow-through and the batch dissolution experiments can be converted to mass of samples loss based on the chemical stoichiometry of the minerals. For tailings samples, the cumulative  $[Mg^{2+}]$  is compared with the total  $Mg^{2+}$  content in the pulp sample to calculate the fraction of the  $Mg^{2+}$  reacted. The sample weight used in both the batch and flow-through dissolution experiments is 500mg. Sample mass loss before and after the experiment is dependent on the extent of dissolution. Mass loss calculated based on aqueous  $[Mg^{2+}]$  agrees with measured mass loss by  $\pm$  5mg in all experiments except for specific cases. Sample mass loss during transfer and recovery of the post-experimental material occurred, which lead to a significant drop in sample weight. In these cases, the mass balance calculation test result was not used for data quality checks and assurance. Mass balance calculation was not applied to all batch dissolution experiments because of the large errors that may occur during transport and recovery of the solid sample. Mass balance calculations from the flowthrough dissolution experiment are summarized in Table 4.13, Appendix B.2.

#### A.2 Charge balance model

Solution charge balance is a relationship describing the balance between the positively charged and negatively charged ions in solution. In aqueous chemistry, solutions must be electrically neutral; that is for every substance of the positive charge, there must be an equivalent amount of negative charge to balance it out. The relationship between effluent [Mg<sup>2+</sup>] and pH from each flow-through dissolution experiments fits a simple charge balance model given certain assumptions and equilibrium constraints. Brucite and serpentine dissolution in an aqueous environment can be modelled as the release of Mg<sup>2+</sup> and OH<sup>-</sup> ions to balance H<sup>+</sup> in solution (Azizi and Larachi, 2019). This simple charge balance model hypothesizes that Mg<sup>2+</sup> is the dominant Mg species and that there are no other significant ions released during dissolution. Magnesium hydroxyl-carbonates (MgHCO<sub>3</sub><sup>+</sup>) are also present at a minor amount and initiate the mineral carbonation reactions (Azizi and Larachi, 2019). In a system at 0.1 bar pCO<sub>2</sub>(g), carbon is present predominantly as  $H_2CO_3$  and  $HCO_3^-$ ; other carbonate species are insignificant and thus neglected. Similarly, a solution with H<sub>3</sub>PO<sub>4</sub> at the same pH range is dominant with H<sub>2</sub>PO<sub>4</sub><sup>2-</sup> ligands. Due to the low abundance of dissolved species, activities are equated to concentration and water activity is set to 1. In the case of mineral dissolution in HCl and HNO<sub>3</sub>, H<sup>+</sup> is the dominating source for acidity. Equilibrium constants for water dissociation, bicarbonate and biphosphate formation are taken from the Wateq database at 25°C from PHREEQC. The change in [Mg<sup>2+</sup>] with [H<sup>+</sup>] reflects solution charge balance from mineral dissolution in various acids, which means the charge balance relationship offers a check for whether the dissolution reaction proceeds as predicted. The charge balance model of different acid (graph of [Mg<sup>2+</sup>] versus [H<sup>+</sup>]) and various pCO<sub>2</sub> content is plotted in Figure 4.1 and Figure 4.2.

The total carbon content in solution with 0.1 bar pCO<sub>2</sub> is  $3.48 \times 10^{-3}$  mol L<sup>-1</sup> (41.8 ppm), verified via geochemical modelling in PHREEQC using the Wateq database (Parkhurst & Appelo, 2013). Activities are equated to concentrations. Gaseous CO<sub>2</sub> dissolving in solution produces H<sub>2</sub>CO<sub>3(aq)</sub>, HCO<sub>3<sup>-</sup>(aq)</sub> and CO<sub>3<sup>2-</sup>(aq)</sub> together with Mg<sup>2+</sup> and MgHCO<sub>3<sup>+</sup></sub> to buffer pH. This multi-step reaction can be simplified based on (Azizi and Larachi, 2019) as follow:

The charge balance relationship is derived as:

Eq 2. 
$$[Mg^{2+}] = \frac{10^{-14}}{2[H^+]} + \frac{(3.981*10^{-3})/2}{(2.212*10^6)*[H^+]+1} - \frac{1}{2}*[H^+]$$

For experiments conducted using HNO<sub>3</sub> and HCl, the charge balance is between the NO<sub>3</sub><sup>-</sup> from the HNO<sub>3</sub> and the Cl<sup>-</sup> present in the HCl. Both HNO<sub>3</sub> and HCl are strong acids with a pKa>1, which allows them to dissociate in solution fully and releases H<sup>+</sup> to generate acidity. Mineral dissolution of brucite and serpentine releases Mg<sup>2+</sup> and buffers the solution pH by consuming H<sup>+</sup>. Lower  $[Mg^{2+}]$  is required for increasing  $[H^+]$  in solution charge balance involving HCl and HNO<sub>3</sub> compare to 0.1 bar pCO<sub>2</sub>.

The reactions are as follow:

 $HNO_3 \rightarrow H^+ + NO_3^-$ 

 $Mg(OH)_2 + H^+ \rightarrow Mg^{2+} + H_2O$ 

 $Mg^{2+} + 2 HNO_3 \rightarrow Mg(NO_3)_2 + H_2$ 

The charge balance relationship is derived as:

Eq 3. 
$$[Mg^{2+}] = \frac{10^{-14}}{2[H^+]} + \frac{[NO_3^-]}{2} - \frac{[H^+]}{2}$$

Finally, for experiments conducted using  $H_3PO_4$ , the ionic concentration solution is  $3.48 \times 10^{-5}$  mol L<sup>-1</sup>, dominated by  $[H_2PO_4^{-1}]$  and  $[HPO_4^{2-}]$ . The reaction and the charge balance model can be declared as:

 $H_2PO_{4^-} \rightarrow H^+ + HPO_{4^{2^-}}$  $Mg(OH)_2 + H^+ \rightarrow Mg^{2+} + H_2O$  $Mg^{2+} + HPO_{4^{2^-}} \rightarrow MgPO_4 + H^+$ 

The charge balance relationship is derived as:

Eq 4. 
$$[Mg^{2+}] = \frac{10^{-14}}{2[H^+]} + \frac{3.981 \times 10^{-5} [H^+] + 4.936 \times 10^{-12}}{(2.212 \times 10^6) \times [H^+] + 1} - \frac{[H^+]}{2}$$



Figure 4.1 PHREEQC modelled trends of [Mg<sup>2+</sup>] versus solution pH, [H<sup>+</sup>] mol L<sup>-1</sup> by dissolving Mg(OH)<sub>2</sub> in 0.1 bar pCO<sub>2</sub>, H<sub>3</sub>PO<sub>4</sub>, HCl and HNO<sub>3</sub> solution.



Figure 4.2 PHREEQC modelled trends of [Mg<sup>2+</sup>] versus solution pH, [H<sup>+</sup>] mol L<sup>-1</sup> by dissolving Mg(OH)<sub>2</sub> in solution at 1 bar pCO<sub>2</sub>, 0.1 bar pCO<sub>2</sub>, 0.0004 bar pCO<sub>2</sub>.

#### Appendix B Supplementary material of chapter 2

#### **B.1** Detailed analyses

# **B.1.1** Particle size distribution and surface area analysis

The initial surface area of each size fraction of the brucite ore used in the experiments was determined by multi-point BET with N<sub>2</sub> adsorption using a Quantachrome Autosorb-1 surface area analyzer. Particle size distribution analysis was performed using a Malvern Mastersizer 2000 Laser Diffraction Particle Size Analyzer on prepared sample particles. Ultrasound of 15s, the 30s and 60s interval is applied to avoid measurement errors due to particle clustering (i.e., very fine and fine size fractions), and value between d(0.8) and d(0.9) is chosen to represent the particle size range of the measured sample.

## **B.1.2** X-ray powder diffraction methods

Natural and synthetic mineral phases in all solid samples were identified using X-ray powder diffraction methods (XRPD). Aliquots were ground under ethanol for three minutes using a McCrone® micronizing mill and agate grinding elements. Micronized aliquots were dried for ~24 h and gently disaggregated with an agate mortar and pestle. Powder mounts were prepared against the ground glass to minimize preferred orientation. Quantitative phase analysis using Rietveld refinement was performed on aliquots of the initial natural brucite, natural quartz, natural serpentinite, synthetic forsterite and two tailings samples (Figure 4.5-4.9).

All XRPD data were collected using a Bruker D8 Focus Bragg-Brentano diffractometer with CoK $\alpha$  radiation and a step size of 0.04° over a range of 3-80°2 $\theta$  at 0.2s/step. Fe monochromator foil, 0.6 mm divergence slit, incident and diffracted beam soller slits, and a Lynx Eye detector were used. A long fine focus Co X-ray tube was operated at 35 kV and 40 mA using a take-off angle of 6°. A rotation speed of 50 rpm was utilized for the collection of qualitative data. Search-match software by Bruker (DIFFRACplusEVA 14; Bruker AXS, 2008) was used for phase identification with reference to the International Centre for Diffraction Database PDF-4+ 2010. Rietveld refinement for quantitative phase analysis was completed using Topaz Version 3 (Bruker AXS, 2004) refinement software.

## **B.1.3** Aqueous chemistry

Total aqueous Al, Ca, Fe, K, Na, Si and Mg concentration was determined using inductively coupled plasma optical emission spectrometry (ICP-OES) using a Varian 725-ES Optical Emission Spectrometer. We analyze certified reference materials (CRM) along with our samples. We process the CRMs the same way as the samples. The CRMs used is QCS-27 ICP 27 element Quality Control Standard from High-Purity Standards. The CRMs helped determined the error on the method or analysis. The detection limit is equivalent to 3 standard deviations of the background and is reported in Table 2.5. Cation samples were acidified to 2% ultrapure HNO<sub>3</sub> immediately the following sampling. The relative errors are determined by using the following formula and expressed as:

Relative error  $=\frac{(x-x0)}{x}$ 

Where, x = true value of prepared standard [Mg]ppm,

 $x_0$  = measured value of [Mg]ppm,

 $x - x_0 = absolute error,$ 

Percent relative error (%) = Relative error  $\times$  100

Relative errors on Mg measurement from each experiment is reported in Table 2.6 in chapter

#### **B.1.4** Comparison with literature data

Many studies have devoted to describing the pH-dependence of the steady-state dissolution kinetics of brucite (Jordan and Rammensee, 1996; Palandri and Kharaka, 2004; Pokrovsky and Schott, 2004; Vermilyea, 1969). The study of natural brucite dissolution in batch reactor performed by Vermilyea (1969) revealed strong pH dependence and is higher than the rate measured by others. Jordan and Ramensee (1996), using Scanning Force Microscopy, determined that brucite dissolution at pH 2.7 is around 10<sup>-6</sup> mol Mg m<sup>-2</sup> s<sup>-1</sup>. Palandri and Kharaka (2004) summarized the results from the three studies and reinterpreted the reaction rates based on the solution mechanism being acid, neutral or base (Figure 4.3). Pokrovsky and Schott., 2004 measured dissolution and precipitation rate of brucite at 25 °C in a mixed-flow reactor as a function of pH (2.5 to 12). Brucite dissolution rates measured by different authors are different, and some achieved orders of magnitude differences (Figure 4.3). Factors that may contribute to the disagreements between measured rates of brucite dissolution include 1) the adopted dissolution kinetics models, 2) the experimental set-up, and 3) measurements of mineral reactive surface area. Each of these factors is discussed in the context of our results.

Firstly, Pokrovsky and Schott (2004) quantified the brucite reaction rate by monitoring surface detachment of  $Mg^{2+}$  without measuring H<sup>+</sup> consumption. Vermilyea (1969), on the other hand, quantified the removal of H<sup>+</sup> without computing the flux of dissolved  $Mg^{2+}$ . As part of the experimental data quality assurance and quality check procedure in this study, a charge balance mode that corresponds to aqueous [H<sup>+</sup>] with [Mg<sup>2+</sup>] is applied. The quantified reaction rate in this study is thus, dependent on both the amount of Mg<sup>2+</sup> removal and the change in pH.

Secondly, in terms of the experimental setup, Pokrovsky and Schott, (2004) used a mixedflow reactor with stirring, while Vermilyea (1969) adopted a batch dissolution reactor. Jordan and
Ramensee (1996) used SEM to measure the dissolution rate based on the change in brucite morphology. The present study performed flow-through dissolution experiments using a 1.2 ml flow-through reactor. All four studies used different experimental set up to measure the brucite dissolution rate. The stirred reactor in Pokrovsky and Schott (2004) could contribute to the formation of ultrafine particles that may enhance the rate of dissolution. The solutions in Vermilyea's batch reactor are continuously buffered, which could lead to mineral saturation and retard dissolution rate. The flow-through reactor will form small effluent pH gradients due to the formation of a "packed-bed sample." The acidic effluent reacting with the top layer will be buffered before accessing the sample at the bottom, contribute to uncertainties when calculating the reaction rate.

Finally, the normalization of measured rates (mol Mg m<sup>-2</sup> s<sup>-1</sup>) to the surface area presents severe problems for direct comparison between rate measurements (Figure 4.3). Vermilyea (1969) calculated reactive surface area from particle size, assuming the particle surface was smooth. Pokrovsky and Schott (2004) and the present study measured mineral reactive surface area using the multi-point BET method. Although the brucite in Polrovsky's study has comparable grain size (50-200um) to the brucite in this study, their surface areas are significantly different. The BET reactive surface area of the brucite used by Pokrovsky and Schott (2004) is determined using krypton absorption (0.204 m<sup>2</sup> g<sup>-1</sup>), while the present study used Nitrogen. Reactive surface area measurements obtained using the "Brunauer–Emmett–Teller" (BET) method can vary significantly depending on the molecular/atomic size of the gas used (e.g., N<sub>2</sub>, Kr, CO<sub>2</sub>) (Hodson, 2006). The atomic radius of Kr molecules is more massive than N<sub>2</sub> by about 25%; thus, it can significantly contribute to the variation in the resulting measurements (Hodson, 2006; Rimstidt et al., 2012; Sing, 2001). Recalculating and comparing the measured rate by various authors based

on sample weight in the unit of mol Mg g<sup>-1</sup> s<sup>-1</sup> shows that the rate measured by Pokrovsky and Schott (2004) and this study converged (Figure 4.4). Although the brucite dissolution rate from Palandri and Kharaka (2004) also agrees well with the rate in this study, there is no explanation for the 100 fold discrepancy of the rate and the fit to Vermilyea (1969) and Jordan and Ramensee (1996)'s data. Comparison of the brucite dissolution rate based on sample weight yield much better results. The reactive surface area of minerals should be noted when computing the rate of reaction.



Figure 4.3 Summary of literature data on the brucite dissolution rate (mol m<sup>-2</sup> s<sup>-1</sup>) at 25° C as a function of pH.



Figure 4.4 Summary of literature data on the brucite dissolution rate (mol g<sup>-1</sup> s<sup>-1</sup>) at 25° C as a function of pH.

## **B.2** Detailed results

## **B.2.1** XRD of sample characterization



Figure 4.5 Representative X-ray diffraction pattern and Rietveld refinement plot of the unreacted brucite sample.



Figure 4.6 Representative X-ray diffraction pattern and Rietveld refinement plot of the unreacted quartz sample.



Figure 4.7 Representative X-ray diffraction pattern and Rietveld refinement plot of the unreacted serpentine sample.



Figure 4.8 Representative X-ray diffraction pattern and Rietveld refinement plot of the unreacted solid of BD-FPCOM.



Figure 4.9 Representative X-ray diffraction pattern and Rietveld refinement plot of the unreacted solid of GK-PK21.

## **B.2.2** Flow-through dissolution experimental data

Time (h)	[Mg <sup>2+</sup> ] mol/l	Cumulative Mg (mol)	Fraction Reacted%	Reaction Rate (mol Mg m <sup>-2</sup> s <sup>-1</sup> )	Reaction Rate (mol Mg g <sup>-1</sup> s <sup>-1</sup> )	Effluent pH	[H <sup>+</sup> ] mol/l	Effluent Saturation Index
0.1	1.21E-03	1.57E-05	2%	9.88E-08	4.10E-07	4.696	2.34E-09	-6.96
0.6	7.08E-04	3.69E-05	5%	5.95E-08	2.47E-07	4.693	4.22E-07	-7.61
1.1	6.27E-04	5.57E-05	8%	5.40E-08	2.24E-07	4.692	7.18E-07	-7.76
1.6	5.57E-04	7.25E-05	10%	4.90E-08	2.03E-07	4.691	8.78E-07	-7.91
2.1	5.20E-04	8.81E-05	12%	4.67E-08	1.94E-07	4.690	9.59E-07	-7.99
2.6	4.89E-04	1.03E-04	14%	4.49E-08	1.86E-07	4.689	1.04E-06	-8.07
3.1	4.50E-04	1.16E-04	16%	4.20E-08	1.74E-07	4.689	1.10E-06	-8.17
3.6	4.46E-04	1.30E-04	18%	4.24E-08	1.76E-07	4.688	1.12E-06	-8.19
4.1	4.11E-04	1.42E-04	19%	3.98E-08	1.65E-07	4.688	1.20E-06	-8.29
4.6	4.23E-04	1.55E-04	21%	4.18E-08	1.73E-07	4.687	1.24E-06	-8.25
5.6	4.10E-04	1.79E-04	24%	4.20E-08	1.75E-07	4.687	1.30E-06	-8.29
6.6	4.01E-04	2.03E-04	28%	4.27E-08	1.77E-07	4.687	1.33E-06	-8.32
7.6	4.11E-04	2.28E-04	31%	4.56E-08	1.89E-07	4.687	1.34E-06	-8.29
8.6	4.04E-04	2.52E-04	34%	4.66E-08	1.94E-07	4.687	1.33E-06	
9.6	3.95E-04	2.76E-04	38%	4.75E-08	1.97E-07	4.686	1.34E-06	
10.6	3.83E-04	2.99E-04	41%	4.81E-08	2.00E-07	4.686	1.41E-06	-8.38
11.6	3.81E-04	3.22E-04	44%	5.01E-08	2.08E-07	4.686	1.42E-06	-8.38
12.6	3.66E-04	3.44E-04	47%	5.02E-08	2.09E-07	4.687	1.37E-06	
13.6	3.76E-04	3.66E-04	50%	5.40E-08	2.24E-07	4.689	1.27E-06	-8.38
14.6	3.72E-04	3.89E-04	53%	5.62E-08	2.33E-07	4.690	1.11E-06	

Table 4.1 Dissolution data of Experiment 19 brucite react in solution at 0.1bar pCO<sub>2</sub>.

15.6	3.64E-04	4.10E-04	56%	5.78E-08	2.40E-07	4.689	1.07E-06	-8.39
16.6	3.78E-04	4.33E-04	59%	6.35E-08	2.64E-07	4.690	1.11E-06	-8.39
17.6	3.60E-04	4.55E-04	62%	6.40E-08	2.66E-07	4.690	1.01E-06	
18.6	3.42E-04	4.75E-04	65%	6.42E-08	2.67E-07	4.690	1.04E-06	
19.6	3.35E-04	4.95E-04	67%	6.68E-08	2.77E-07	4.690	1.00E-06	-8.37
20.6	3.36E-04	5.15E-04	70%	7.13E-08	2.96E-07	4.690	9.87E-07	-8.37
21.6	3.31E-04	5.35E-04	73%	7.49E-08	3.11E-07	4.689	1.02E-06	
22.6	3.21E-04	5.55E-04	75%	7.78E-08	3.23E-07	4.689	1.08E-06	
23.6	3.02E-04	5.73E-04	78%	7.83E-08	3.25E-07	4.688	1.16E-06	
24.6	2.86E-04	5.90E-04	80%	7.96E-08	3.30E-07	4.686	1.26E-06	-8.74
25.6	2.70E-04	6.06E-04	82%	8.06E-08	3.34E-07	4.684	1.40E-06	-8.74
26.6	2.58E-04	6.21E-04	85%	8.28E-08	3.44E-07	4.682	1.59E-06	
27.6	2.40E-04	6.36E-04	86%	8.29E-08	3.44E-07	4.677	1.81E-06	
29.6	1.95E-04	6.59E-04	90%	7.66E-08	3.18E-07	4.671	2.28E-06	
31.6	1.62E-04	6.79E-04	92%	7.18E-08	2.98E-07	4.662	2.83E-06	-9.45
33.6	1.54E-04	6.97E-04	95%	7.78E-08	3.23E-07	4.651	3.70E-06	-9.51
35.6	9.89E-05	7.09E-04	96%	5.49E-08	2.28E-07	4.641	4.84E-06	
37.6	7.72E-05	7.18E-04	98%	4.64E-08	1.93E-07	4.628	5.92E-06	
39.6	5.90E-05	7.26E-04	99%	3.79E-08	1.57E-07	4.613	7.34E-06	-10.67
41.6	4.60E-05	7.31E-04	99%	3.12E-08	1.30E-07	4.606	8.90E-06	
43.6	3.75E-05	7.36E-04	100%	2.67E-08	1.11E-07	4.594	9.70E-06	-11.17
45.6	3.16E-05	7.39E-04	101%	2.34E-08	9.72E-08	4.573	1.12E-05	
47.6	2.40E-05	7.42E-04	101%	1.83E-08	7.62E-08	4.545	1.37E-05	
49.6	1.74E-05	7.44E-04	101%	1.36E-08	5.66E-08	4.533	1.71E-05	-11.88
51.6	1.25E-05	7.46E-04	101%	1.00E-08	4.15E-08	4.526	1.88E-05	

53.6	9.52E-06	7.47E-04	102%	7.71E-09	3.20E-08	4.513	1.98E-05	-12.30
55.6	7.43E-06	7.48E-04	102%	6.08E-09	2.52E-08	4.499	2.16E-05	-12.44
57.6	5.28E-06	7.48E-04	102%	4.36E-09	1.81E-08	4.491	2.36E-05	
59.6	3.96E-06	7.49E-04	102%	3.28E-09	1.36E-08	4.486	2.48E-05	
61.6	2.52E-06	7.49E-04	102%	2.10E-09	8.72E-09	4.486	2.55E-05	
63.6	1.86E-06	7.49E-04	102%	1.55E-09	6.44E-09	4.481	2.56E-05	-13.18
65.6	1.16E-06	7.50E-04	102%	9.69E-10	4.02E-09	4.485	2.63E-05	
67.6	6.80E-07	7.50E-04	102%	5.70E-10	2.37E-09	4.482	2.56E-05	
69.6	3.99E-07	7.50E-04	102%	3.34E-10	1.39E-09	4.474	2.61E-05	
71.6	5.55E-08	7.50E-04	102%	4.66E-11	1.93E-10		2.74E-05	-14.75
73.6	7.40E-08	7.50E-04	102%	6.21E-11	2.58E-10	4.458	2.81E-05	-14.62
75.6	-4.24E-07	7.50E-04	102%	-3.55E-10	-1.47E-09	4.453	2.99E-05	
77.6	-1.03E-06	7.50E-04	102%	-8.58E-10	-3.56E-09	4.450	3.07E-05	
79.6	-1.17E-06	7.49E-04	102%	-9.78E-10	-4.06E-09	4.447	3.12E-05	
81.6	-1.46E-06	7.49E-04	102%	-1.22E-09	-5.05E-09	4.440	3.17E-05	
83.6	-9.18E-07	7.49E-04	102%	-7.64E-10	-3.17E-09	4.440	3.28E-05	
85.6	-1.82E-06	7.49E-04	102%	-1.51E-09	-6.28E-09	4.438	3.29E-05	
87.6	-2.05E-06	7.49E-04	102%	-1.70E-09	-7.05E-09	4.440	3.31E-05	
89.6	-2.14E-06	7.48E-04	102%	-1.76E-09	-7.32E-09	4.448	3.27E-05	
91.6	-2.28E-06	7.48E-04	102%	-1.87E-09	-7.76E-09	4.452	3.15E-05	
93.6	-2.09E-06	7.48E-04	102%	-1.71E-09	-7.11E-09	4.446	3.08E-05	
95.6	-2.07E-06	7.48E-04	102%	-1.69E-09	-7.03E-09	4.440	3.18E-05	
97.6	-2.17E-06	7.47E-04	102%	-1.76E-09	-7.32E-09	4.436	3.29E-05	
99.6	-2.31E-06	7.47E-04	102%	-1.88E-09	-7.78E-09	4.400	3.35E-05	

Time (h)	[Mg <sup>2+</sup> ] mol/l	Cumulative Mg (mol)	Fraction Reacted%	Reaction Rate (mol Mg m <sup>-2</sup> s <sup>-1</sup> )	Reaction Rate (mol Mg g <sup>-1</sup> s <sup>-1</sup> )	Effluent pH	[H⁺] mol/l	Effluent Saturation Index
0.11	6.86E-04	8.92E-06	1%	5.57E-08	2.31E-07	4.701	2.63E-11	2.71
0.61	2.68E-04	1.70E-05	2%	2.20E-08	9.11E-08	4.701	4.25E-11	1.49
1.11	2.22E-04	2.36E-05	3%	1.83E-08	7.61E-08	4.701	5.08E-11	1.23
1.61	2.00E-04	2.96E-05	4%	1.67E-08	6.92E-08	4.701	5.69E-11	1.09
2.11	1.84E-04	3.51E-05	5%	1.54E-08	6.41E-08	4.701	6.27E-11	0.98
2.61	1.66E-04	4.01E-05	5%	1.40E-08	5.81E-08	4.701	6.88E-11	0.84
3.11	1.54E-04	4.47E-05	6%	1.31E-08	5.44E-08	4.701	7.57E-11	0.73
3.61	1.38E-04	4.89E-05	7%	1.18E-08	4.91E-08	4.701	8.35E-11	0.58
4.11	1.30E-04	5.28E-05	7%	1.12E-08	4.63E-08	4.701	9.15E-11	0.49
4.61	1.17E-04	5.63E-05	8%	1.00E-08	4.17E-08	4.701	1.01E-10	0.34
5.11	1.10E-04	5.96E-05	8%	9.52E-09	3.95E-08	4.701	1.11E-10	0.25
6.11	9.79E-05	6.55E-05	9%	8.53E-09	3.54E-08	4.701	1.33E-10	0.08
7.11	8.27E-05	7.04E-05	10%	7.26E-09	3.01E-08	4.701	1.58E-10	-0.18
8.11	7.26E-05	7.48E-05	10%	6.40E-09	2.66E-08	4.701	1.87E-10	-0.39
9.11	7.95E-05	7.96E-05	11%	7.07E-09	2.93E-08	4.701	2.19E-10	-0.24
10.11	6.84E-05	8.37E-05	11%	6.11E-09	2.53E-08	4.701	2.53E-10	-0.49
11.11	5.84E-05	8.72E-05	12%	5.24E-09	2.17E-08	4.701	2.89E-10	-0.75
12.11	5.74E-05	9.06E-05	12%	5.18E-09	2.15E-08	4.701	3.28E-10	-0.78
13.11	5.28E-05	9.38E-05	13%	4.78E-09	1.99E-08	4.701	3.74E-10	-0.93
14.11	4.99E-05	9.68E-05	13%	4.53E-09	1.88E-08	4.701	4.24E-10	-1.03
15.11	5.22E-05	9.99E-05	14%	4.77E-09	1.98E-08	4.701	4.82E-10	-0.95
16.11	4.69E-05	1.03E-04	14%	4.30E-09	1.78E-08	4.701	5.38E-10	-1.15
17.11	4.65E-05	1.05E-04	14%	4.27E-09	1.77E-08	4.701	6.08E-10	-1.17
18.11	4.31E-05	1.08E-04	15%	3.98E-09	1.65E-08	4.701	6.86E-10	-1.32
19.11	4.50E-05	1.11E-04	15%	4.17E-09	1.73E-08	4.701	7.83E-10	-1.23
20.11	4.30E-05	1.13E-04	15%	4.00E-09	1.66E-08	4.701	8.55E-10	
21.11	4.13E-05	1.16E-04	16%	3.86E-09	1.60E-08	4.701	9.38E-10	

Table 4.2 Dissolution data of Experiment 12 brucite react in solution with HCl.

22.11	3.99E-05	1.18E-04	16%	3.74E-09	1.55E-08	4.701	1.04E-09	
23.11	3.87E-05	1.21E-04	16%	3.63E-09	1.51E-08	4.701	1.14E-09	-1.55
24.11	3.82E-05	1.23E-04	17%	3.60E-09	1.49E-08	4.701	1.24E-09	
26.11	4.40E-05	1.28E-04	17%	4.18E-09	1.73E-08	4.701	1.40E-09	
28.11	4.46E-05	1.33E-04	18%	4.27E-09	1.77E-08	4.701	1.64E-09	
30.11	5.08E-05	1.40E-04	19%	4.90E-09	2.04E-08	4.701	1.91E-09	
32.11	3.65E-05	1.44E-04	20%	3.55E-09	1.47E-08	4.701	2.29E-09	-1.68
34.11	4.03E-05	1.49E-04	20%	3.95E-09	1.64E-08	4.701	2.82E-09	
36.11	6.06E-05	1.56E-04	21%	5.99E-09	2.49E-08	4.701	3.45E-09	
38.11	3.44E-05	1.60E-04	22%	3.42E-09	1.42E-08	4.701	4.16E-09	
40.11	3.39E-05	1.64E-04	22%	3.39E-09	1.41E-08	4.701	4.82E-09	
42.11	3.32E-05	1.68E-04	23%	3.35E-09	1.39E-08	4.701	5.83E-09	-1.91
44.11	3.36E-05	1.72E-04	23%	3.41E-09	1.41E-08	4.701	6.33E-09	
46.11	3.42E-05	1.76E-04	24%	3.49E-09	1.45E-08	4.701	6.16E-09	
48.11	3.55E-05	1.81E-04	25%	3.64E-09	1.51E-08	4.701	6.17E-09	
50.11	3.51E-05	1.85E-04	25%	3.63E-09	1.51E-08	4.701	7.04E-09	
52.11	3.25E-05	1.89E-04	26%	3.38E-09	1.40E-08	4.701	7.45E-09	-1.97
54.11	3.21E-05	1.93E-04	26%	3.36E-09	1.40E-08	4.701	8.66E-09	
56.11	3.22E-05	1.96E-04	27%	3.39E-09	1.41E-08	4.701	9.13E-09	
58.11	3.20E-05	2.00E-04	27%	3.39E-09	1.41E-08	4.701	1.16E-08	
60.11	3.21E-05	2.04E-04	28%	3.41E-09	1.42E-08	4.701	1.54E-08	
62.11	3.19E-05	2.08E-04	28%	3.42E-09	1.42E-08	4.701	1.98E-08	-2.02
64.11	3.14E-05	2.12E-04	29%	3.38E-09	1.40E-08	4.701	2.21E-08	
66.11	2.95E-05	2.15E-04	29%	3.20E-09	1.33E-08	4.701	2.76E-08	
68.11	2.86E-05	2.19E-04	30%	3.12E-09	1.30E-08	4.701	3.50E-08	
70.11	2.84E-05	2.22E-04	30%	3.11E-09	1.29E-08	4.701	2.69E-08	
72.11	2.86E-05	2.26E-04	31%	3.16E-09	1.31E-08	4.701	2.46E-08	-2.34
74.11	2.86E-05	2.29E-04	31%	3.17E-09	1.32E-08	4.701	2.10E-08	
76.11	2.82E-05	2.32E-04	32%	3.15E-09	1.31E-08	4.701	2.08E-08	
78.11	2.93E-05	2.36E-04	32%	3.29E-09	1.36E-08	4.701	6.12E-09	
80.11	2.85E-05	2.39E-04	33%	3.22E-09	1.34E-08	4.701	1.82E-08	

82.11	2.78E-05	2.43E-04	33%	3.16E-09	1.31E-08	4.701	2.19E-08	-2.44
84.11	2.79E-05	2.46E-04	33%	3.19E-09	1.32E-08	4.701	2.78E-08	
86.11	2.72E-05	2.49E-04	34%	3.12E-09	1.29E-08	4.701	3.65E-08	
88.11	2.69E-05	2.52E-04	34%	3.10E-09	1.29E-08	4.700	3.78E-08	
90.11	2.64E-05	2.56E-04	35%	3.06E-09	1.27E-08	4.700	5.07E-08	
92.11	2.55E-05	2.59E-04	35%	2.98E-09	1.23E-08	4.700	5.23E-08	
94.11	2.63E-05	2.62E-04	36%	3.09E-09	1.28E-08	4.701	5.01E-08	-2.64
96.11	2.62E-05	2.65E-04	36%	3.09E-09	1.28E-08	4.701	4.16E-08	
98.11	2.61E-05	2.68E-04	36%	3.10E-09	1.29E-08	4.701	4.11E-08	
100.11	2.58E-05	2.71E-04	37%	3.08E-09	1.28E-08	4.700	4.61E-08	
102.11	2.51E-05	2.74E-04	37%	3.02E-09	1.25E-08	4.700	6.68E-08	-2.83
104.11	2.52E-05	2.77E-04	38%	3.04E-09	1.26E-08	4.700	7.40E-08	
106.11	2.49E-05	2.80E-04	38%	3.02E-09	1.25E-08	4.700	1.12E-07	-2.88

Table 4.3 Dissolution data of Experiment 8 brucite react in solution with HCl.

Time (h)	[Mg <sup>2+</sup> ] mol/l	Cumulative Mg (mol)	Fraction Reacted%	Reaction Rate (mol Mg m <sup>-2</sup> s <sup>-1</sup> )	Reaction Rate (mol Mg g <sup>-1</sup> s <sup>-1</sup> )	Effluent pH	[H⁺] mol/l	Effluent Saturation Index
0.1	5.82E-04	7.57E-06	1%	7.09E-08	1.96E-07	4.701	5.05E-11	2.50
0.6	2.30E-04	1.45E-05	2%	2.61E-08	7.82E-08	4.701	5.78E-11	1.28
1.1	1.96E-04	2.04E-05	3%	2.17E-08	6.69E-08	4.701	7.33E-11	1.06
1.6	1.63E-04	2.52E-05	3%	1.74E-08	5.60E-08	4.701	8.81E-11	0.81
2.1	1.39E-04	2.94E-05	4%	1.54E-08	4.80E-08	4.701	1.02E-10	0.59
2.6	1.24E-04	3.31E-05	5%	1.35E-08	4.32E-08	4.701	1.17E-10	0.42
3.1	1.12E-04	3.65E-05	5%	1.27E-08	3.91E-08	4.701	1.31E-10	0.27
3.6	1.05E-04	3.96E-05	5%	1.18E-08	3.67E-08	4.701	1.47E-10	0.18
4.1	9.63E-05	4.25E-05	6%	1.09E-08	3.38E-08	4.701	1.63E-10	0.05
4.6	9.17E-05	4.53E-05	6%	9.57E-09	3.23E-08	4.701	1.81E-10	-0.02
5.1	8.53E-05	4.78E-05	7%	9.39E-09	3.02E-08	4.701	1.97E-10	-0.13
5.6	8.06E-05	5.03E-05	7%	9.21E-09	2.86E-08	4.701	2.17E-10	-0.22

6.1	7.69E-05	5.26E-05	7%	8.42E-09	2.74E-08	4.701	2.35E-10	-0.30
6.6	7.66E-05	5.49E-05	7%	7.97E-09	2.73E-08	4.701	2.57E-10	-0.30
7.6	6.58E-05	5.88E-05	8%	7.53E-09	2.36E-08	4.701	3.12E-10	-0.55
8.6	6.25E-05	6.26E-05	9%	6.78E-09	2.25E-08	4.701	3.83E-10	-0.64
9.6	5.85E-05	6.61E-05	9%	6.36E-09	2.12E-08	4.701	4.58E-10	-0.75
10.6	5.54E-05	6.94E-05	9%	6.04E-09	2.02E-08	4.701	5.45E-10	-0.84
11.6	5.22E-05	7.25E-05	10%	6.05E-09	1.91E-08	4.701	6.54E-10	-0.95
12.6	5.01E-05	7.55E-05	10%	5.67E-09	1.84E-08	4.701	7.94E-10	-1.03
13.6	4.83E-05	7.84E-05	11%	5.28E-09	1.78E-08	4.701	9.63E-10	-1.09
14.6	4.66E-05	8.12E-05	11%	5.21E-09	1.72E-08	4.701	1.14E-09	-1.16
15.6	4.52E-05	8.39E-05	11%	5.06E-09	1.68E-08	4.701	1.39E-09	
16.6	4.38E-05	8.66E-05	12%	5.04E-09	1.63E-08	4.701	1.74E-09	-1.29
17.6	4.23E-05	8.91E-05	12%	4.98E-09	1.58E-08	4.701	2.19E-09	
18.6	4.20E-05	9.16E-05	12%	4.89E-09	1.57E-08	4.701	2.39E-09	
19.6	4.18E-05	9.41E-05	13%	4.70E-09	1.57E-08	4.701	2.56E-09	
20.6	4.18E-05	9.67E-05	13%	4.90E-09	1.58E-08	4.701	2.94E-09	
21.6	3.66E-05	9.89E-05	13%	4.42E-09	1.39E-08	4.701	2.68E-09	-1.67
22.6	3.59E-05	1.01E-04	14%	4.49E-09	1.36E-08	4.701	3.37E-09	
23.6	4.10E-05	1.03E-04	14%	4.04E-09	1.56E-08	4.701	4.14E-09	
25.6	3.45E-05	1.08E-04	15%	4.04E-09	1.32E-08	4.701	7.73E-09	
27.6	3.46E-05	1.12E-04	15%	3.93E-09	1.33E-08	4.701	1.74E-08	
29.6	3.32E-05	1.16E-04	16%	3.89E-09	1.29E-08	4.700	3.97E-08	-1.91
31.6	3.15E-05	1.20E-04	16%	3.89E-09	1.23E-08	4.699	8.89E-08	
33.6	3.10E-05	1.23E-04	17%	3.67E-09	1.22E-08	4.699	1.42E-07	
35.6	2.99E-05	1.27E-04	17%	3.64E-09	1.18E-08	4.698	1.96E-07	
37.6	2.95E-05	1.30E-04	18%	3.48E-09	1.17E-08	4.697	2.62E-07	
39.6	2.80E-05	1.34E-04	18%	3.26E-09	1.11E-08	4.697	3.69E-07	-2.41
41.6	2.74E-05	1.37E-04	19%	3.35E-09	1.10E-08	4.698	4.11E-07	
43.6	2.79E-05	1.40E-04	19%	3.47E-09	1.12E-08	4.698	3.20E-07	
45.6	2.79E-05	1.44E-04	20%	3.50E-09	1.12E-08	4.697	3.23E-07	
47.6	2.69E-05	1.47E-04	20%	3.38E-09	1.09E-08	4.697	3.47E-07	

49.6	2.76E-05	1.50E-04	20%	3.43E-09	1.12E-08	4.697	3.57E-07	-2.46
51.6	2.70E-05	1.54E-04	21%	3.17E-09	1.10E-08	4.697	4.14E-07	
53.6	2.72E-05	1.57E-04	21%	3.20E-09	1.12E-08	4.697	3.82E-07	
55.6	2.86E-05	1.60E-04	22%	3.33E-09	1.18E-08	4.698	3.28E-07	
57.6	2.86E-05	1.64E-04	22%	3.41E-09	1.19E-08	4.698	3.13E-07	
59.6	2.92E-05	1.67E-04	23%	3.31E-09	1.22E-08	4.698	2.99E-07	-2.28
61.6	2.75E-05	1.70E-04	23%	3.63E-09	1.15E-08	4.698	2.85E-07	
65.6	3.32E-05	1.74E-04	24%	3.38E-09	1.40E-08	4.698	2.54E-07	
67.6	3.19E-05	1.78E-04	24%	3.40E-09	1.36E-08	4.699	2.10E-07	-2.02
69.6	3.13E-05	1.82E-04	25%	3.47E-09	1.34E-08	4.699	2.00E-07	-2.07

Table 4.4 Dissolution data of Experiment 16 brucite react in solution with H<sub>3</sub>PO<sub>4</sub>.

Time (h)	[Mg <sup>2+</sup> ] mol/l	Cumulative Mg (mol)	Fraction Reacted%	Reaction Rate (mol Mg m <sup>-2</sup> s <sup>-1</sup> )	Reaction Rate (mol Mg g <sup>-1</sup> s <sup>-1</sup> )	Effluent pH	[H <sup>+</sup> ] mol/l	Effluent Saturation Index
0.1	4.81E-04	6.25E-06	1%	3.89E-08	1.61E-07	4.701	6.86E-11	2.21
0.6	1.43E-04	1.05E-05	1%	1.16E-08	4.81E-08	4.701	1.62E-10	0.47
1.1	1.15E-04	1.40E-05	2%	9.41E-09	3.91E-08	4.701	2.42E-10	0.10
1.6	1.03E-04	1.71E-05	2%	8.44E-09	3.50E-08	4.701	2.99E-10	-0.09
2.1	9.94E-05	2.01E-05	3%	8.18E-09	3.39E-08	4.701	3.71E-10	-0.16
2.6	9.40E-05	2.29E-05	3%	7.76E-09	3.22E-08	4.701	4.32E-10	-0.26
3.1	9.07E-05	2.56E-05	3%	7.51E-09	3.12E-08	4.701	5.22E-10	-0.33
3.6	8.48E-05	2.81E-05	4%	7.04E-09	2.92E-08	4.701	6.09E-10	-0.47
4.1	8.14E-05	3.06E-05	4%	6.78E-09	2.81E-08	4.701	7.34E-10	-0.55
4.6	7.97E-05	3.30E-05	4%	6.66E-09	2.76E-08	4.701	8.99E-10	-0.60
5.6	7.49E-05	3.75E-05	5%	6.29E-09	2.61E-08	4.701	1.39E-09	-0.73
6.6	6.89E-05	4.16E-05	6%	5.81E-09	2.41E-08	4.701	2.47E-09	-0.93
7.6	6.60E-05	4.56E-05	6%	5.60E-09	2.32E-08	4.701	4.89E-09	-1.04
8.6	6.07E-05	4.92E-05	7%	5.17E-09	2.15E-08	4.701	9.70E-09	-1.27
9.6	5.76E-05	5.27E-05	7%	4.93E-09	2.05E-08	4.701	1.74E-08	-1.43

10.6	5.49E-05	5.60E-05	8%	4.72E-09	1.96E-08	4.701	2.89E-08	-1.59
11.6	5.16E-05	5.91E-05	8%	4.45E-09	1.85E-08	4.701	3.81E-08	
12.6	4.95E-05	6.20E-05	8%	4.29E-09	1.78E-08	4.700	4.86E-08	
13.6	4.82E-05	6.49E-05	9%	4.19E-09	1.74E-08	4.700	5.67E-08	-2.14
14.6	4.68E-05	6.77E-05	9%	4.08E-09	1.69E-08	4.700	6.39E-08	
15.6	4.67E-05	7.05E-05	10%	4.09E-09	1.70E-08	4.700	7.22E-08	
16.6	4.45E-05	7.32E-05	10%	3.91E-09	1.62E-08	4.700	7.96E-08	
17.6	4.30E-05	7.58E-05	10%	3.79E-09	1.57E-08	4.700	8.73E-08	
18.6	4.23E-05	7.83E-05	11%	3.74E-09	1.55E-08	4.700	9.56E-08	-3.11
19.6	4.19E-05	8.08E-05	11%	3.71E-09	1.54E-08	4.700	9.55E-08	
20.6	4.15E-05	8.33E-05	11%	3.69E-09	1.53E-08	4.700	9.49E-08	
21.6	4.15E-05	8.58E-05	12%	3.70E-09	1.54E-08	4.700	9.82E-08	
22.6	4.06E-05	8.82E-05	12%	3.64E-09	1.51E-08	4.700	9.86E-08	
23.6	4.05E-05	9.07E-05	12%	3.64E-09	1.51E-08	4.700	1.02E-07	-3.66
24.6	4.02E-05	9.31E-05	13%	3.62E-09	1.50E-08	4.700	1.06E-07	
26.6	4.02E-05	9.79E-05	13%	3.64E-09	1.51E-08	4.700	1.12E-07	
28.6	3.88E-05	1.03E-04	14%	3.54E-09	1.47E-08	4.700	1.19E-07	
30.6	3.93E-05	1.07E-04	15%	3.61E-09	1.50E-08	4.699	1.31E-07	
32.6	3.82E-05	1.12E-04	15%	3.52E-09	1.46E-08	4.699	1.43E-07	-4.51
34.6	3.63E-05	1.16E-04	16%	3.38E-09	1.40E-08	4.699	1.71E-07	
36.6	3.90E-05	1.21E-04	16%	3.65E-09	1.51E-08	4.699	2.01E-07	
38.6	3.69E-05	1.25E-04	17%	3.47E-09	1.44E-08	4.698	2.21E-07	
40.6	3.72E-05	1.30E-04	18%	3.52E-09	1.46E-08	4.698	2.45E-07	
42.6	3.58E-05	1.34E-04	18%	3.41E-09	1.42E-08	4.698	2.70E-07	-5.21
44.6	3.53E-05	1.38E-04	19%	3.38E-09	1.40E-08	4.698	2.56E-07	
46.6	3.55E-05	1.43E-04	19%	3.42E-09	1.42E-08	4.698	2.73E-07	
48.6	3.38E-05	1.47E-04	20%	3.27E-09	1.36E-08	4.697	2.94E-07	
50.6	3.39E-05	1.51E-04	20%	3.30E-09	1.37E-08	4.697	3.33E-07	
52.6	3.24E-05	1.55E-04	21%	3.18E-09	1.32E-08	4.696	4.13E-07	-5.94
54.6	3.24E-05	1.58E-04	22%	3.19E-09	1.33E-08	4.695	4.59E-07	
56.6	3.22E-05	1.62E-04	22%	3.19E-09	1.32E-08	4.692	6.02E-07	

58.6	3.04E-05	1.66E-04	23%	3.03E-09	1.26E-08	4.690	8.59E-07	
60.6	2.95E-05	1.70E-04	23%	2.95E-09	1.23E-08	4.687	1.06E-06	
62.6	2.80E-05	1.73E-04	24%	2.82E-09	1.17E-08	4.685	1.29E-06	-6.76
64.6	2.73E-05	1.76E-04	24%	2.76E-09	1.15E-08	4.682	1.54E-06	
66.6	2.66E-05	1.79E-04	24%	2.70E-09	1.12E-08	4.681	1.80E-06	
68.6	2.71E-05	1.83E-04	25%	2.76E-09	1.15E-08	4.678	1.87E-06	
70.6	2.63E-05	1.86E-04	25%	2.70E-09	1.12E-08	4.675	2.15E-06	
72.6	2.53E-05	1.89E-04	26%	2.60E-09	1.08E-08	4.670	2.42E-06	-7.32
74.6	2.54E-05	1.92E-04	26%	2.63E-09	1.09E-08	4.665	2.91E-06	
76.6	2.45E-05	1.95E-04	26%	2.55E-09	1.06E-08	4.658	3.47E-06	
78.6	2.44E-05	1.98E-04	27%	2.55E-09	1.06E-08	4.650	4.13E-06	
80.6	2.36E-05	2.01E-04	27%	2.47E-09	1.03E-08	4.632	4.99E-06	
82.6	2.29E-05	2.03E-04	28%	2.41E-09	1.00E-08	4.617	6.87E-06	-7.96
84.6	2.17E-05	2.06E-04	28%	2.29E-09	9.50E-09	4.602	8.53E-06	
86.6	2.14E-05	2.08E-04	28%	2.27E-09	9.41E-09	4.587	1.02E-05	
88.6	2.05E-05	2.11E-04	29%	2.18E-09	9.06E-09	4.576	1.19E-05	
90.6	1.98E-05	2.13E-04	29%	2.11E-09	8.78E-09	4.567	1.32E-05	
92.6	1.96E-05	2.16E-04	29%	2.10E-09	8.73E-09	4.562	1.44E-05	-9.54
94.6	1.80E-05	2.18E-04	30%	1.94E-09	8.06E-09	4.555	1.50E-05	
96.6	1.80E-05	2.20E-04	30%	1.94E-09	8.05E-09	4.543	1.59E-05	
98.6	1.74E-05	2.22E-04	30%	1.88E-09	7.81E-09	4.538	1.75E-05	
100.6	1.65E-05	2.24E-04	30%	1.79E-09	7.44E-09	4.525	1.82E-05	
102.6	1.58E-05	2.26E-04	31%	1.72E-09	7.14E-09	4.525	1.98E-05	-10.95
104.6	1.56E-05	2.28E-04	31%	1.70E-09	7.06E-09	4.526	1.97E-05	

Time (h)	[Mg <sup>2+</sup> ] mol/l	Cumulative Mg (mol)	Fraction Reacted %	Reaction Rate (mol Mg m <sup>-2</sup> s <sup>-1</sup> )	Reaction Rate (mol Mg g <sup>-1</sup> s <sup>-1</sup> )	Effluent pH	[H <sup>+</sup> ] mol/l	Mg/Si
0.11	7.86E-04	1.02E-05	0%	4.72E-10	2.62E-08	4.686	2.27E-07	13.85
0.61	3.17E-04	2.18E-05	0%	1.91E-10	1.06E-08	4.673	1.38E-06	5.66
1.11	1.95E-04	2.89E-05	1%	1.18E-10	6.53E-09	4.662	2.64E-06	4.81
1.61	1.51E-04	3.44E-05	1%	9.14E-11	5.08E-09	4.653	3.73E-06	4.43
2.11	1.26E-04	3.90E-05	1%	7.63E-11	4.24E-09	4.646	4.66E-06	4.27
2.61	1.10E-04	4.30E-05	1%	6.64E-11	3.69E-09	4.639	5.42E-06	4.07
3.11	9.92E-05	4.66E-05	1%	6.01E-11	3.34E-09	4.633	6.14E-06	3.73
3.61	8.75E-05	4.98E-05	1%	5.30E-11	2.94E-09	4.624	6.71E-06	3.68
4.61	7.13E-05	5.46E-05	1%	4.32E-11	2.40E-09	4.615	7.77E-06	3.36
5.61	7.03E-05	5.93E-05	1%	4.27E-11	2.37E-09	4.608	8.72E-06	3.15
6.61	6.32E-05	6.35E-05	1%	3.84E-11	2.13E-09	4.604	9.47E-06	2.99
7.61	5.76E-05	6.73E-05	1%	3.50E-11	1.95E-09	4.598	9.96E-06	2.96
8.61	5.49E-05	7.09E-05	1%	3.34E-11	1.85E-09	4.593	1.06E-05	2.91
9.61	5.11E-05	7.43E-05	1%	3.11E-11	1.73E-09	4.585	1.13E-05	2.78
10.61	4.68E-05	7.74E-05	1%	2.85E-11	1.58E-09	4.580	1.21E-05	2.75
11.61	4.48E-05	8.04E-05	1%	2.73E-11	1.52E-09	4.575	1.28E-05	2.70
12.61	4.21E-05	8.32E-05	2%	2.56E-11	1.42E-09	4.570	1.34E-05	2.47
13.61	3.94E-05	8.58E-05	2%	2.40E-11	1.33E-09	4.566	1.40E-05	2.56
14.61	3.88E-05	8.84E-05	2%	2.37E-11	1.32E-09	4.562	1.45E-05	2.43
15.61	3.52E-05	9.08E-05	2%	2.15E-11	1.19E-09	4.558	1.50E-05	2.53
16.61	3.43E-05	9.30E-05	2%	2.09E-11	1.16E-09	4.555	1.56E-05	2.40
17.61	3.35E-05	9.53E-05	2%	2.04E-11	1.14E-09	4.552	1.59E-05	2.35
18.61	3.22E-05	9.74E-05	2%	1.97E-11	1.09E-09	4.558	1.63E-05	2.29
19.61	3.43E-05	9.97E-05	2%	2.10E-11	1.17E-09	4.567	1.55E-05	2.30
20.61	3.62E-05	1.02E-04	2%	2.21E-11	1.23E-09	4.570	1.44E-05	2.19
21.61	3.43E-05	1.04E-04	2%	2.10E-11	1.17E-09	4.573	1.40E-05	2.27
22.61	3.96E-05	1.07E-04	2%	2.42E-11	1.35E-09	4.575	1.37E-05	2.21

Table 4.5 Dissolution data of Experiment 10 serpentine react in solution at 0.1 bar pCO<sub>2</sub>.

23.61	3.90E-05	1.10E-04	2%	2.39E-11	1.33E-09	4.570	1.35E-05	2.20
24.61	3.60E-05	1.12E-04	2%	2.21E-11	1.23E-09	4.567	1.40E-05	2.19
25.61	3.70E-05	1.14E-04	2%	2.27E-11	1.26E-09	4.559	1.44E-05	2.11
27.61	3.29E-05	1.19E-04	2%	2.02E-11	1.12E-09	4.556	1.54E-05	2.06
29.61	3.13E-05	1.23E-04	2%	1.92E-11	1.07E-09	4.561	1.58E-05	2.09
31.61	3.59E-05	1.27E-04	2%	2.21E-11	1.23E-09	4.560	1.52E-05	2.09
33.61	3.37E-05	1.31E-04	2%	2.07E-11	1.15E-09	4.545	1.52E-05	2.07
35.61	3.25E-05	1.36E-04	3%	2.00E-11	1.11E-09	4.539	1.72E-05	2.03
37.61	2.84E-05	1.39E-04	3%	1.75E-11	9.71E-10	4.534	1.80E-05	2.02
39.61	2.84E-05	1.43E-04	3%	1.75E-11	9.74E-10	4.529	1.87E-05	1.83
41.61	2.55E-05	1.46E-04	3%	1.57E-11	8.73E-10	4.534	1.94E-05	1.94
43.61	2.51E-05	1.49E-04	3%	1.55E-11	8.62E-10	4.552	1.87E-05	1.91
45.61	3.02E-05	1.53E-04	3%	1.87E-11	1.04E-09	4.558	1.62E-05	1.87
47.61	3.13E-05	1.57E-04	3%	1.93E-11	1.07E-09	4.560	1.55E-05	1.84
49.61	3.15E-05	1.61E-04	3%	1.95E-11	1.08E-09	4.557	1.52E-05	1.90
51.61	2.90E-05	1.65E-04	3%	1.80E-11	9.98E-10	4.554	1.57E-05	1.87
53.61	2.95E-05	1.68E-04	3%	1.83E-11	1.01E-09	4.550	1.60E-05	1.86
55.61	2.78E-05	1.72E-04	3%	1.73E-11	9.58E-10	4.546	1.66E-05	1.90
57.61	2.71E-05	1.75E-04	3%	1.68E-11	9.34E-10	4.538	1.70E-05	1.80
59.61	2.65E-05	1.79E-04	3%	1.65E-11	9.14E-10	4.533	1.82E-05	1.80
63.61	2.45E-05	1.82E-04	3%	1.52E-11	8.43E-10	4.530	1.92E-05	1.88
65.61	2.16E-05	1.84E-04	3%	1.34E-11	7.44E-10	4.528	1.95E-05	1.82
67.61	2.48E-05	1.88E-04	3%	1.54E-11	8.55E-10	4.536	1.85E-05	1.74
69.61	2.55E-05	1.91E-04	4%	1.59E-11	8.82E-10	4.549	1.67E-05	1.76
71.61	2.85E-05	1.94E-04	4%	1.78E-11	9.86E-10	4.553	1.61E-05	1.86
73.61	2.66E-05	1.98E-04	4%	1.66E-11	9.21E-10	4.551	1.64E-05	1.79
75.61	2.71E-05	2.01E-04	4%	1.69E-11	9.37E-10	4.547	1.69E-05	1.71
77.61	2.74E-05	2.05E-04	4%	1.71E-11	9.49E-10	4.550	1.65E-05	1.74

Time (h)	[Mg <sup>2+</sup> ] mol/l	Cumulative Mg (mol)	Fraction Reacted%	Reaction Rate (mol Mg m <sup>-2</sup> s <sup>-1</sup> )	Reaction Rate (mol Mg g <sup>-1</sup> s <sup>-1</sup> )	Effluent pH	[H <sup>+</sup> ] mol/l	Mg/Si
0.11	4.95E-04	6.44E-06	0%	2.98E-10	1.65E-08	4.701	7.09E-10	12.26
0.61	9.12E-05	9.17E-06	0%	5.49E-11	3.05E-09	4.701	2.56E-10	3.84
1.11	6.77E-05	1.12E-05	0%	4.07E-11	2.26E-09	4.701	2.72E-10	3.59
1.61	5.62E-05	1.29E-05	0%	3.38E-11	1.88E-09	4.701	3.09E-10	3.49
2.11	5.07E-05	1.44E-05	0%	3.05E-11	1.69E-09	4.701	3.54E-10	3.28
2.61	4.70E-05	1.58E-05	0%	2.83E-11	1.57E-09	4.701	4.01E-10	3.27
3.11	4.38E-05	1.71E-05	0%	2.64E-11	1.47E-09	4.701	4.47E-10	3.39
3.61	4.19E-05	1.84E-05	0%	2.52E-11	1.40E-09	4.701	4.95E-10	3.32
4.11	4.05E-05	1.96E-05	0%	2.44E-11	1.36E-09	4.701	5.50E-10	3.12
5.11	3.70E-05	2.18E-05	0%	2.23E-11	1.24E-09	4.701	6.56E-10	3.31
6.11	3.61E-05	2.40E-05	1%	2.18E-11	1.21E-09	4.701	7.82E-10	3.03
7.11	3.31E-05	2.60E-05	1%	2.00E-11	1.11E-09	4.701	9.43E-10	2.86
8.11	3.07E-05	2.78E-05	1%	1.85E-11	1.03E-09	4.701	1.13E-09	2.99
9.11	2.97E-05	2.96E-05	1%	1.79E-11	9.95E-10	4.701	1.35E-09	2.97
10.11	2.97E-05	3.14E-05	1%	1.79E-11	9.95E-10	4.701	1.67E-09	2.85
11.11	2.94E-05	3.31E-05	1%	1.78E-11	9.86E-10	4.701	2.10E-09	2.99
12.11	2.79E-05	3.48E-05	1%	1.68E-11	9.34E-10	4.701	2.72E-09	2.97
13.11	2.77E-05	3.65E-05	1%	1.67E-11	9.29E-10	4.701	3.58E-09	3.07
14.11	2.42E-05	3.79E-05	1%	1.46E-11	8.13E-10	4.701	4.99E-09	3.06
15.11	2.73E-05	3.96E-05	1%	1.65E-11	9.16E-10	4.701	7.47E-09	2.78
16.11	2.53E-05	4.11E-05	1%	1.53E-11	8.50E-10	4.701	1.25E-08	2.87
17.11	2.56E-05	4.26E-05	1%	1.55E-11	8.61E-10	4.700	2.41E-08	2.98
18.11	2.52E-05	4.41E-05	1%	1.52E-11	8.47E-10	4.700	5.14E-08	2.77
19.11	2.49E-05	4.56E-05	1%	1.51E-11	8.38E-10	4.699	9.89E-08	3.02
20.11	2.42E-05	4.71E-05	1%	1.47E-11	8.14E-10	4.699	1.46E-07	2.69
21.11	2.28E-05	4.85E-05	1%	1.38E-11	7.66E-10	4.699	1.85E-07	3.04
22.11	2.35E-05	4.99E-05	1%	1.42E-11	7.91E-10	4.698	2.20E-07	2.81

Table 4.6 Dissolution data of Experiment 13 serpentine react in solution with HCl.

23.11	2.34E-05	5.13E-05	1%	1.42E-11	7.86E-10	4.698	2.59E-07	2.74
24.11	2.31E-05	5.27E-05	1%	1.40E-11	7.77E-10	4.697	2.97E-07	2.47
25.11	2.31E-05	5.40E-05	1%	1.40E-11	7.77E-10	4.697	3.34E-07	2.52
26.11	2.39E-05	5.55E-05	1%	1.45E-11	8.03E-10	4.696	3.87E-07	2.69
28.11	2.33E-05	5.83E-05	1%	1.42E-11	7.87E-10	4.694	5.01E-07	2.52
30.11	2.23E-05	6.10E-05	1%	1.36E-11	7.53E-10	4.691	6.70E-07	3.16
32.11	2.01E-05	6.34E-05	1%	1.22E-11	6.80E-10	4.689	8.93E-07	2.53
34.11	4.82E-05	6.91E-05	1%	2.93E-11	1.63E-09	4.685	1.13E-06	3.04
36.11	1.96E-05	7.15E-05	2%	1.19E-11	6.62E-10	4.681	1.49E-06	2.53
38.11	1.92E-05	7.38E-05	2%	1.17E-11	6.49E-10	4.676	1.90E-06	2.33
40.11	1.90E-05	7.61E-05	2%	1.16E-11	6.42E-10	4.670	2.39E-06	1.82
42.11	1.87E-05	7.83E-05	2%	1.14E-11	6.32E-10	4.663	2.97E-06	2.24
44.11	1.80E-05	8.05E-05	2%	1.10E-11	6.09E-10	4.659	3.61E-06	2.27
46.11	1.74E-05	8.26E-05	2%	1.06E-11	5.88E-10	4.655	4.08E-06	2.24
48.11	1.91E-05	8.49E-05	2%	1.16E-11	6.45E-10	4.652	4.45E-06	2.48
50.11	1.82E-05	8.70E-05	2%	1.11E-11	6.15E-10	4.647	4.73E-06	2.27
52.11	1.61E-05	8.90E-05	2%	9.83E-12	5.46E-10	4.642	5.24E-06	2.30
54.11	1.85E-05	9.12E-05	2%	1.13E-11	6.27E-10	4.634	5.82E-06	2.57
56.11	1.66E-05	9.32E-05	2%	1.01E-11	5.63E-10	4.625	6.67E-06	2.08
58.11	1.78E-05	9.53E-05	2%	1.09E-11	6.04E-10	4.616	7.59E-06	2.48
60.11	1.51E-05	9.71E-05	2%	9.22E-12	5.12E-10	4.607	8.62E-06	2.18
62.11	1.55E-05	9.90E-05	2%	9.46E-12	5.26E-10	4.600	9.58E-06	2.25
64.11	1.72E-05	1.01E-04	2%	1.05E-11	5.84E-10	4.594	1.04E-05	2.59
66.11	1.65E-05	1.03E-04	2%	1.01E-11	5.61E-10	4.591	1.11E-05	2.10
68.11	1.36E-05	1.05E-04	2%	8.35E-12	4.64E-10	4.591	1.15E-05	2.14
70.11	1.50E-05	1.06E-04	2%	9.19E-12	5.11E-10	4.594	1.15E-05	1.99
72.11	1.43E-05	1.08E-04	2%	8.75E-12	4.86E-10	4.595	1.11E-05	2.11
74.11	1.42E-05	1.10E-04	2%	8.73E-12	4.85E-10	4.593	1.10E-05	2.26
76.11	1.47E-05	1.12E-04	2%	9.00E-12	5.00E-10	4.591	1.12E-05	2.13
78.11	1.29E-05	1.13E-04	2%	7.88E-12	4.38E-10	4.586	1.15E-05	1.92
80.11	1.31E-05	1.15E-04	2%	8.01E-12	4.45E-10	4.581	1.21E-05	1.83

82.11	1.28E-05	1.16E-04	2%	7.85E-12	4.36E-10	4.576	1.27E-05	2.15
84.11	1.29E-05	1.18E-04	3%	7.89E-12	4.38E-10	4.573	1.32E-05	2.10
86.11	2.09E-05	1.20E-04	3%	1.28E-11	7.13E-10	4.569	1.37E-05	2.72
88.11	1.26E-05	1.22E-04	3%	7.72E-12	4.29E-10	4.566	1.41E-05	2.14
90.11	1.22E-05	1.23E-04	3%	7.47E-12	4.15E-10	4.565	1.45E-05	1.88
92.11	1.26E-05	1.25E-04	3%	7.73E-12	4.29E-10	4.569	1.46E-05	2.04
94.11	1.32E-05	1.26E-04	3%	8.11E-12	4.50E-10	4.572	1.42E-05	2.28
96.11	1.26E-05	1.28E-04	3%	7.75E-12	4.30E-10	4.575	1.37E-05	1.90
98.11	1.52E-05	1.30E-04	3%	9.35E-12	5.19E-10	4.575	1.34E-05	2.20
100.11	1.24E-05	1.31E-04	3%	7.62E-12	4.23E-10	4.573	1.34E-05	2.06
102.11	1.22E-05	1.33E-04	3%	7.50E-12	4.16E-10	4.573	1.37E-05	1.79

Table 4.7 Dissolution data of Experiment 14 serpentine react in solution with HNO<sub>3</sub>.

Time (h)	[Mg <sup>2+</sup> ] mol/l	Cumulative Mg (mol)	Fraction Reacted%	Reaction Rate (mol Mg m <sup>-2</sup> s <sup>-1</sup> )	Reaction Rate (mol Mg g <sup>-1</sup> s <sup>-1</sup> )	Effluent pH	[H <sup>+</sup> ] mol/l	Mg/Si
0.1	4.31E-04	5.60E-06	0%	2.59E-10	1.44E-08	4.701	1.08E-09	12.26
0.6	8.44E-05	8.13E-06	0%	5.07E-11	2.82E-09	4.701	2.58E-10	3.84
1.1	6.14E-05	9.97E-06	0%	3.69E-11	2.05E-09	4.701	2.53E-10	3.59
1.6	5.36E-05	1.16E-05	0%	3.22E-11	1.79E-09	4.701	2.72E-10	3.49
2.1	4.61E-05	1.30E-05	0%	2.77E-11	1.54E-09	4.701	2.99E-10	3.28
2.6	4.41E-05	1.43E-05	0%	2.66E-11	1.48E-09	4.701	3.33E-10	3.27
3.1	4.28E-05	1.56E-05	0%	2.58E-11	1.43E-09	4.701	3.73E-10	3.39
3.6	3.99E-05	1.68E-05	0%	2.40E-11	1.34E-09	4.701	4.18E-10	3.32
4.1	3.73E-05	1.79E-05	0%	2.25E-11	1.25E-09	4.701	4.62E-10	3.12
4.6	3.57E-05	1.90E-05	0%	2.15E-11	1.19E-09	4.701	5.08E-10	3.31
5.6	3.26E-05	2.09E-05	0%	1.97E-11	1.09E-09	4.701	6.24E-10	3.03
6.6	3.05E-05	2.27E-05	0%	1.84E-11	1.02E-09	4.701	7.70E-10	2.86
7.6	2.94E-05	2.45E-05	1%	1.77E-11	9.84E-10	4.701	9.46E-10	2.99
8.6	2.79E-05	2.62E-05	1%	1.68E-11	9.33E-10	4.701	1.15E-09	2.97

10.6 2.76E-05 2.94E-05 1% 1.67E-11 9.26E-10   11.6 2.59E-05 3.10E-05 1% 1.56E-11 8.68E-10   12.6 2.52E-05 3.25E-05 1% 1.52E-11 8.45E-10   13.6 2.46E-05 3.40E-05 1% 1.49E-11 8.25E-10   14.6 2.38E-05 3.54E-05 1% 1.44E-11 7.98E-10   15.6 2.77E-05 3.71E-05 1% 1.41E-11 7.82E-10   16.6 2.33E-05 3.85E-05 1% 1.41E-11 7.82E-10   17.6 2.27E-05 3.98E-05 1% 1.36E-11 7.63E-10   18.6 2.25E-05 4.12E-05 1% 1.36E-11 7.68E-10   19.6 2.29E-05 4.26E-05 1% 1.31E-11 7.26E-10   21.6 2.17E-05 4.52E-05 1% 1.31E-11 7.20E-10   22.6 2.17E-05 4.52E-05 1% 1.31E-11 7.20E-10   23.6 2.09E-05 5.21E-05 1% 1.26E-11 6.95E-10   24.6 3.17E-	4.701	1.44E-09	2.85
11.6 2.59E-05 3.10E-05 1% 1.56E-11 8.68E-10   12.6 2.52E-05 3.25E-05 1% 1.52E-11 8.45E-10   13.6 2.46E-05 3.40E-05 1% 1.49E-11 8.25E-10   14.6 2.38E-05 3.54E-05 1% 1.44E-11 7.98E-10   15.6 2.77E-05 3.71E-05 1% 1.68E-11 9.31E-10   16.6 2.33E-05 3.85E-05 1% 1.41E-11 7.82E-10   17.6 2.27E-05 3.98E-05 1% 1.36E-11 7.63E-10   18.6 2.25E-05 4.12E-05 1% 1.36E-11 7.68E-10   19.6 2.29E-05 4.26E-05 1% 1.31E-11 7.26E-10   21.6 2.17E-05 4.52E-05 1% 1.31E-11 7.30E-10   22.6 2.17E-05 4.52E-05 1% 1.31E-11 7.30E-10   23.6 2.09E-05 1% 1.31E-11 7.02E-10 1.07E-09   26.6 2.07E-05 5.21E-05 1% 1.92E-11 6.07E-05   28.6 1.96E-	4.701	1.80E-09	2.99
12.6 2.52E-05 3.25E-05 1% 1.52E-11 8.45E-10   13.6 2.46E-05 3.40E-05 1% 1.49E-11 8.25E-10   14.6 2.38E-05 3.54E-05 1% 1.44E-11 7.98E-10   15.6 2.77E-05 3.71E-05 1% 1.68E-11 9.31E-10   16.6 2.33E-05 3.85E-05 1% 1.41E-11 7.82E-10   17.6 2.27E-05 3.98E-05 1% 1.37E-11 7.63E-10   18.6 2.25E-05 4.12E-05 1% 1.36E-11 7.54E-10   19.6 2.29E-05 4.26E-05 1% 1.31E-11 7.68E-10   20.6 2.16E-05 4.39E-05 1% 1.31E-11 7.26E-10   21.6 2.17E-05 4.65E-05 1% 1.31E-11 7.02E-10   23.6 2.09E-05 4.52E-05 1% 1.31E-11 7.02E-10   24.6 3.17E-05 4.65E-05 1% 1.31E-11 6.95E-10   24.6 3.17E-05 5.21E-05 1% 1.25E-11 6.95E-10   26.6 1.96E-	4.701	2.31E-09	2.97
13.6 2.46E-05 3.40E-05 1% 1.49E-11 8.25E-10   14.6 2.38E-05 3.54E-05 1% 1.44E-11 7.98E-10   15.6 2.77E-05 3.71E-05 1% 1.68E-11 9.31E-10   16.6 2.33E-05 3.85E-05 1% 1.41E-11 7.82E-10   17.6 2.27E-05 3.98E-05 1% 1.37E-11 7.63E-10   18.6 2.25E-05 4.12E-05 1% 1.36E-11 7.54E-10   19.6 2.29E-05 4.26E-05 1% 1.31E-11 7.26E-10   20.6 2.16E-05 4.39E-05 1% 1.31E-11 7.26E-10   21.6 2.17E-05 4.52E-05 1% 1.31E-11 7.30E-10   22.6 2.17E-05 4.65E-05 1% 1.31E-11 7.02E-10   23.6 2.09E-05 4.77E-05 1% 1.26E-11 7.02E-10   24.6 3.17E-05 5.21E-05 1% 1.25E-11 6.46E-10   26.6 1.90E-05 5.47E-05 1% 1.07E-11 5.95E-10   36.6 1.90E-	4.701	3.01E-09	3.07
14.6 2.38E-05 3.54E-05 1% 1.44E-11 7.98E-10   15.6 2.77E-05 3.71E-05 1% 1.68E-11 9.31E-10   16.6 2.33E-05 3.85E-05 1% 1.41E-11 7.82E-10   17.6 2.27E-05 3.98E-05 1% 1.37E-11 7.63E-10   18.6 2.25E-05 4.12E-05 1% 1.36E-11 7.54E-10   19.6 2.29E-05 4.26E-05 1% 1.31E-11 7.68E-10   20.6 2.16E-05 4.39E-05 1% 1.31E-11 7.26E-10   21.6 2.17E-05 4.52E-05 1% 1.31E-11 7.29E-10   22.6 2.17E-05 4.65E-05 1% 1.31E-11 7.02E-10   24.6 3.17E-05 4.65E-05 1% 1.26E-11 7.02E-10   24.6 3.17E-05 5.21E-05 1% 1.25E-11 6.95E-10   26.6 2.07E-05 5.45E-05 1% 1.19E-11 6.61E-10   30.6 1.90E-05 5.67E-05 1% 1.09E-11 6.61E-10   30.6 1.90E-	4.701	4.01E-09	3.06
15.6 2.77E-05 3.71E-05 1% 1.68E-11 9.31E-10   16.6 2.33E-05 3.85E-05 1% 1.41E-11 7.82E-10   17.6 2.27E-05 3.98E-05 1% 1.37E-11 7.63E-10   18.6 2.25E-05 4.12E-05 1% 1.36E-11 7.54E-10   19.6 2.29E-05 4.26E-05 1% 1.31E-11 7.26E-10   21.6 2.16E-05 4.39E-05 1% 1.31E-11 7.26E-10   21.6 2.17E-05 4.52E-05 1% 1.31E-11 7.29E-10   22.6 2.17E-05 4.65E-05 1% 1.31E-11 7.29E-10   23.6 2.09E-05 4.77E-05 1% 1.31E-11 7.02E-10   24.6 3.17E-05 4.96E-05 1% 1.26E-11 7.02E-10   24.6 1.96E-05 5.21E-05 1% 1.25E-11 6.95E-10   28.6 1.96E-05 5.45E-05 1% 1.19E-11 6.61E-10   30.6 1.90E-05 5.67E-05 1% 1.09E-11 5.95E-10   34.6 1.70E-	4.701	5.53E-09	2.78
16.6 2.33E-05 3.85E-05 1% 1.41E-11 7.82E-10   17.6 2.27E-05 3.98E-05 1% 1.37E-11 7.63E-10   18.6 2.25E-05 4.12E-05 1% 1.36E-11 7.54E-10   19.6 2.29E-05 4.26E-05 1% 1.38E-11 7.68E-10   20.6 2.16E-05 4.39E-05 1% 1.31E-11 7.26E-10   21.6 2.17E-05 4.52E-05 1% 1.31E-11 7.30E-10   22.6 2.17E-05 4.65E-05 1% 1.31E-11 7.30E-10   23.6 2.09E-05 4.77E-05 1% 1.26E-11 7.02E-10   24.6 3.17E-05 4.96E-05 1% 1.25E-11 6.95E-10   28.6 1.96E-05 5.21E-05 1% 1.19E-11 6.61E-10   30.6 1.90E-05 5.45E-05 1% 1.19E-11 6.06E-10   34.6 1.70E-05 6.10E-05 1% 1.09E-11 5.95E-10   36.6 1.70E-05 6.30E-05 1% 1.03E-11 5.72E-10   36.6 1.70E-	4.701	7.93E-09	2.87
17.62.27E-053.98E-051%1.37E-117.63E-1018.62.25E-054.12E-051%1.36E-117.54E-1019.62.29E-054.26E-051%1.38E-117.68E-1020.62.16E-054.39E-051%1.31E-117.26E-1021.62.17E-054.52E-051%1.31E-117.29E-1022.62.17E-054.65E-051%1.31E-117.30E-1023.62.09E-054.77E-051%1.26E-117.02E-1024.63.17E-054.96E-051%1.92E-111.07E-0926.62.07E-055.21E-051%1.25E-116.95E-1028.61.96E-055.45E-051%1.19E-116.61E-1030.61.90E-055.67E-051%1.09E-116.06E-1034.61.77E-056.10E-051%1.03E-115.95E-1036.61.70E-056.30E-051%1.03E-115.95E-1036.61.79E-056.51E-051%1.05E-115.97E-1036.61.79E-056.51E-051%1.05E-115.84E-1036.61.79E-056.51E-051%9.68E-125.37E-1036.61.59E-056.89E-051%9.48E-125.27E-1036.61.56E-056.89E-051%9.48E-125.27E-1044.61.61E-057.08E-051%9.54E-125.37E-1044.61.61E-057.08E-051%9.54E-125.30E-10	4.701	1.21E-08	2.98
18.62.25E-054.12E-051%1.36E-117.54E-1019.62.29E-054.26E-051%1.38E-117.68E-1020.62.16E-054.39E-051%1.31E-117.26E-1021.62.17E-054.52E-051%1.31E-117.29E-1022.62.17E-054.65E-051%1.31E-117.30E-1023.62.09E-054.77E-051%1.26E-117.02E-1024.63.17E-054.96E-051%1.92E-111.07E-0926.62.07E-055.21E-051%1.92E-116.95E-1028.61.96E-055.45E-051%1.19E-116.61E-1030.61.90E-055.67E-051%1.15E-116.40E-1032.61.80E-055.89E-051%1.07E-115.95E-1034.61.77E-056.10E-051%1.03E-115.72E-1036.61.70E-056.51E-051%1.03E-115.72E-1038.61.73E-056.51E-051%9.68E-125.37E-1040.61.59E-056.89E-051%9.48E-125.27E-1044.61.61E-057.08E-051%9.48E-125.27E-1044.61.61E-057.08E-051%9.48E-125.27E-1046.61.57E-051%9.48E-125.27E-10	4.701	1.95E-08	2.77
19.62.29E-054.26E-051%1.38E-117.68E-1020.62.16E-054.39E-051%1.31E-117.26E-1021.62.17E-054.52E-051%1.31E-117.29E-1022.62.17E-054.65E-051%1.31E-117.30E-1023.62.09E-054.77E-051%1.26E-117.02E-1024.63.17E-054.96E-051%1.92E-111.07E-0926.62.07E-055.21E-051%1.25E-116.95E-1028.61.96E-055.45E-051%1.19E-116.61E-1030.61.90E-055.67E-051%1.15E-116.06E-1032.61.80E-055.89E-051%1.09E-116.06E-1034.61.77E-056.10E-051%1.07E-115.95E-1036.61.70E-056.30E-051%1.03E-115.72E-1038.61.73E-056.51E-051%9.68E-125.37E-1040.61.59E-056.89E-051%9.48E-125.27E-1044.61.61E-057.08E-051%9.77E-125.43E-10	4.700	3.38E-08	3.02
20.62.16E-054.39E-051%1.31E-117.26E-1021.62.17E-054.52E-051%1.31E-117.29E-1022.62.17E-054.65E-051%1.31E-117.30E-1023.62.09E-054.77E-051%1.26E-117.02E-1024.63.17E-054.96E-051%1.92E-111.07E-0926.62.07E-055.21E-051%1.25E-116.95E-1028.61.96E-055.45E-051%1.19E-116.61E-1030.61.90E-055.67E-051%1.15E-116.40E-1032.61.80E-055.89E-051%1.09E-116.06E-1034.61.77E-056.10E-051%1.07E-115.95E-1036.61.70E-056.30E-051%1.03E-115.72E-1038.61.73E-056.51E-051%1.05E-115.84E-1040.61.59E-056.89E-051%9.68E-125.37E-1044.61.61E-057.08E-051%9.48E-125.27E-1044.61.61E-057.08E-051%9.54E-125.43E-10	4.700	6.33E-08	2.69
21.62.17E-054.52E-051%1.31E-117.29E-1022.62.17E-054.65E-051%1.31E-117.30E-1023.62.09E-054.77E-051%1.26E-117.02E-1024.63.17E-054.96E-051%1.92E-111.07E-0926.62.07E-055.21E-051%1.25E-116.95E-1028.61.96E-055.45E-051%1.19E-116.61E-1030.61.90E-055.67E-051%1.15E-116.40E-1032.61.80E-055.89E-051%1.09E-116.06E-1034.61.77E-056.10E-051%1.07E-115.95E-1036.61.70E-056.30E-051%1.03E-115.72E-1038.61.73E-056.51E-051%1.05E-115.84E-1040.61.59E-056.70E-051%9.68E-125.37E-1044.61.61E-057.08E-051%9.77E-125.43E-1044.61.61E-057.08E-051%9.77E-125.43E-10	4.699	1.09E-07	3.04
22.62.17E-054.65E-051%1.31E-117.30E-1023.62.09E-054.77E-051%1.26E-117.02E-1024.63.17E-054.96E-051%1.92E-111.07E-0926.62.07E-055.21E-051%1.25E-116.95E-1028.61.96E-055.45E-051%1.19E-116.61E-1030.61.90E-055.67E-051%1.15E-116.40E-1032.61.80E-055.89E-051%1.09E-116.06E-1034.61.77E-056.10E-051%1.07E-115.95E-1036.61.70E-056.30E-051%1.03E-115.72E-1038.61.73E-056.51E-051%1.05E-115.84E-1040.61.59E-056.70E-051%9.68E-125.37E-1044.61.61E-057.08E-051%9.77E-125.43E-1044.61.61E-057.08E-051%9.54E-125.37E-10	4.699	1.62E-07	2.81
23.62.09E-054.77E-051%1.26E-117.02E-1024.63.17E-054.96E-051%1.92E-111.07E-0926.62.07E-055.21E-051%1.25E-116.95E-1028.61.96E-055.45E-051%1.19E-116.61E-1030.61.90E-055.67E-051%1.15E-116.40E-1032.61.80E-055.89E-051%1.09E-116.06E-1034.61.77E-056.10E-051%1.07E-115.95E-1036.61.70E-056.30E-051%1.03E-115.72E-1038.61.73E-056.51E-051%1.05E-115.84E-1040.61.59E-056.70E-051%9.68E-125.37E-1042.61.56E-056.89E-051%9.48E-125.27E-1044.61.61E-057.08E-051%9.77E-125.43E-1046.61.57E-057.27E-052%9.54E-125.30E-10	4.698	2.15E-07	2.74
24.63.17E-054.96E-051%1.92E-111.07E-0926.62.07E-055.21E-051%1.25E-116.95E-1028.61.96E-055.45E-051%1.19E-116.61E-1030.61.90E-055.67E-051%1.15E-116.40E-1032.61.80E-055.89E-051%1.09E-116.06E-1034.61.77E-056.10E-051%1.07E-115.95E-1036.61.70E-056.30E-051%1.03E-115.72E-1038.61.73E-056.51E-051%1.05E-115.84E-1040.61.59E-056.70E-051%9.68E-125.37E-1042.61.66E-056.89E-051%9.48E-125.27E-1044.61.61E-057.08E-051%9.77E-125.43E-1046.61.57E-057.27E-052%9.54E-125.30E-10	4.698	2.66E-07	2.47
26.62.07E-055.21E-051%1.25E-116.95E-1028.61.96E-055.45E-051%1.19E-116.61E-1030.61.90E-055.67E-051%1.15E-116.40E-1032.61.80E-055.89E-051%1.09E-116.06E-1034.61.77E-056.10E-051%1.07E-115.95E-1036.61.70E-056.30E-051%1.03E-115.72E-1038.61.73E-056.51E-051%1.05E-115.84E-1040.61.59E-056.70E-051%9.68E-125.37E-1042.61.56E-056.89E-051%9.48E-125.27E-1044.61.61E-057.08E-051%9.77E-125.43E-1046.61.57E-057.27E-052%9.54E-125.30E-10	4.696	3.23E-07	2.52
28.61.96E-055.45E-051%1.19E-116.61E-1030.61.90E-055.67E-051%1.15E-116.40E-1032.61.80E-055.89E-051%1.09E-116.06E-1034.61.77E-056.10E-051%1.07E-115.95E-1036.61.70E-056.30E-051%1.03E-115.72E-1038.61.73E-056.51E-051%1.05E-115.84E-1040.61.59E-056.70E-051%9.68E-125.37E-1042.61.56E-056.89E-051%9.48E-125.27E-1044.61.61E-057.08E-051%9.77E-125.43E-1046.61.57E-057.27E-052%9.54E-125.30E-10	4.694	4.72E-07	2.69
30.61.90E-055.67E-051%1.15E-116.40E-1032.61.80E-055.89E-051%1.09E-116.06E-1034.61.77E-056.10E-051%1.07E-115.95E-1036.61.70E-056.30E-051%1.03E-115.72E-1038.61.73E-056.51E-051%1.05E-115.84E-1040.61.59E-056.70E-051%9.68E-125.37E-1042.61.56E-056.89E-051%9.48E-125.27E-1044.61.61E-057.08E-051%9.77E-125.43E-1046.61.57E-057.27E-052%9.54E-125.30E-10	4.692	6.29E-07	2.52
32.61.80E-055.89E-051%1.09E-116.06E-1034.61.77E-056.10E-051%1.07E-115.95E-1036.61.70E-056.30E-051%1.03E-115.72E-1038.61.73E-056.51E-051%1.05E-115.84E-1040.61.59E-056.70E-051%9.68E-125.37E-1042.61.56E-056.89E-051%9.48E-125.27E-1044.61.61E-057.08E-051%9.77E-125.43E-1046.61.57E-057.27E-052%9.54E-125.30E-10	4.690	8.30E-07	3.16
34.61.77E-056.10E-051%1.07E-115.95E-1036.61.70E-056.30E-051%1.03E-115.72E-1038.61.73E-056.51E-051%1.05E-115.84E-1040.61.59E-056.70E-051%9.68E-125.37E-1042.61.56E-056.89E-051%9.48E-125.27E-1044.61.61E-057.08E-051%9.77E-125.43E-1046.61.57E-057.27E-052%9.54E-125.30E-10	4.687	1.06E-06	2.53
36.61.70E-056.30E-051%1.03E-115.72E-1038.61.73E-056.51E-051%1.05E-115.84E-1040.61.59E-056.70E-051%9.68E-125.37E-1042.61.56E-056.89E-051%9.48E-125.27E-1044.61.61E-057.08E-051%9.77E-125.43E-1046.61.57E-057.27E-052%9.54E-125.30E-10	4.683	1.33E-06	3.04
38.6 1.73E-05 6.51E-05 1% 1.05E-11 5.84E-10   40.6 1.59E-05 6.70E-05 1% 9.68E-12 5.37E-10   42.6 1.56E-05 6.89E-05 1% 9.48E-12 5.27E-10   44.6 1.61E-05 7.08E-05 1% 9.77E-12 5.43E-10   46.6 1.57E-05 7.27E-05 2% 9.54E-12 5.30E-10	4.680	1.64E-06	2.53
40.61.59E-056.70E-051%9.68E-125.37E-1042.61.56E-056.89E-051%9.48E-125.27E-1044.61.61E-057.08E-051%9.77E-125.43E-1046.61.57E-057.27E-052%9.54E-125.30E-10	4.675	2.00E-06	2.33
42.6 1.56E-05 6.89E-05 1% 9.48E-12 5.27E-10   44.6 1.61E-05 7.08E-05 1% 9.77E-12 5.43E-10   46.6 1.57E-05 7.27E-05 2% 9.54E-12 5.30E-10	4.671	2.42E-06	1.82
44.6 1.61E-05 7.08E-05 1% 9.77E-12 5.43E-10   46.6 1.57E-05 7.27E-05 2% 9.54E-12 5.30E-10	4.668	2.89E-06	2.24
46.6 1.57E-05 7.27E-05 2% 9.54E-12 5.30E-10	4.664	3.18E-06	2.27
	4.662	3.49E-06	2.24
48.6 1.58E-05 7.46E-05 2% 9.61E-12 5.34E-10	4.658	3.73E-06	2.48
50.6   1.51E-05   7.64E-05   2%   9.19E-12   5.10E-10	4.655	4.11E-06	2.27
52.6 1.48E-05 7.82E-05 2% 8.99E-12 4.99E-10	4.651	4.44E-06	2.30
54.6 1.49E-05 8.00E-05 2% 9.08E-12 5.04E-10	4.647	4.86E-06	2.57

56.6	1.44E-05	8.17E-05	2%	8.79E-12	4.88E-10	4.640	5.30E-06	2.08
58.6	1.39E-05	8.34E-05	2%	8.45E-12	4.70E-10	4.632	6.06E-06	2.48
60.6	1.36E-05	8.50E-05	2%	8.30E-12	4.61E-10	4.624	6.90E-06	2.18
62.6	1.32E-05	8.66E-05	2%	8.04E-12	4.46E-10	4.617	7.71E-06	2.25
64.6	1.29E-05	8.81E-05	2%	7.87E-12	4.37E-10	4.610	8.55E-06	2.59
66.6	1.28E-05	8.97E-05	2%	7.80E-12	4.33E-10	4.606	9.32E-06	2.10
68.6	1.30E-05	9.12E-05	2%	7.92E-12	4.40E-10	4.605	9.76E-06	2.14
70.6	1.32E-05	9.28E-05	2%	8.07E-12	4.48E-10	4.604	9.90E-06	1.99
72.6	1.32E-05	9.44E-05	2%	8.04E-12	4.46E-10	4.602	1.00E-05	2.11
74.6	1.31E-05	9.60E-05	2%	8.01E-12	4.45E-10	4.599	1.02E-05	2.26
76.6	1.33E-05	9.76E-05	2%	8.13E-12	4.52E-10	4.595	1.06E-05	2.13
78.6	1.24E-05	9.90E-05	2%	7.58E-12	4.21E-10	4.591	1.10E-05	1.92
80.6	1.22E-05	1.01E-04	2%	7.46E-12	4.14E-10	4.587	1.15E-05	1.83
82.6	1.18E-05	1.02E-04	2%	7.20E-12	4.00E-10	4.579	1.20E-05	2.15
84.6	1.16E-05	1.03E-04	2%	7.09E-12	3.94E-10	4.573	1.29E-05	2.10
86.6	1.12E-05	1.05E-04	2%	6.83E-12	3.79E-10	4.568	1.37E-05	2.72
88.6	1.08E-05	1.06E-04	2%	6.63E-12	3.68E-10	4.563	1.43E-05	2.14
90.6	1.08E-05	1.07E-04	2%	6.63E-12	3.68E-10	4.561	1.49E-05	1.88
92.6	1.10E-05	1.09E-04	2%	6.74E-12	3.75E-10	4.566	1.51E-05	2.04
94.6	1.16E-05	1.10E-04	2%	7.12E-12	3.95E-10	4.569	1.46E-05	2.28
96.6	1.18E-05	1.11E-04	2%	7.23E-12	4.02E-10	4.568	1.41E-05	1.90
98.6	1.14E-05	1.13E-04	2%	7.01E-12	3.89E-10	4.568	1.43E-05	2.20

Time (h)	[Mg <sup>2+</sup> ] mol/l	Cumulative Mg (mol)	Fraction Reacted%	Reaction Rate (mol Mg m <sup>-2</sup> s <sup>-1</sup> )	Reaction Rate (mol Mg g <sup>-1</sup> s <sup>-1</sup> )	Effluent pH	[H <sup>+</sup> ] mol/l	Mg/Si
0.11	4.29E-04	5.58E-06	0%	2.58E-10	1.43E-08	4.701	6.64E-10	13.19
0.61	8.39E-05	8.10E-06	0%	5.04E-11	2.80E-09	4.701	2.84E-10	4.20
1.11	6.84E-05	1.01E-05	0%	4.11E-11	2.28E-09	4.701	2.68E-10	4.35
1.61	6.26E-05	1.20E-05	0%	3.77E-11	2.09E-09	4.701	2.80E-10	4.18
2.11	5.80E-05	1.38E-05	0%	3.49E-11	1.94E-09	4.701	2.97E-10	4.35
2.61	5.50E-05	1.54E-05	0%	3.31E-11	1.84E-09	4.701	3.22E-10	4.33
3.11	5.28E-05	1.70E-05	0%	3.18E-11	1.76E-09	4.701	3.53E-10	4.54
3.61	5.29E-05	1.86E-05	0%	3.19E-11	1.77E-09	4.701	3.91E-10	4.27
4.11	5.46E-05	2.02E-05	0%	3.29E-11	1.83E-09	4.701	4.36E-10	4.51
4.61	5.46E-05	2.19E-05	0%	3.29E-11	1.83E-09	4.701	4.99E-10	4.92
5.61	5.18E-05	2.50E-05	1%	3.13E-11	1.74E-09	4.701	6.56E-10	4.58
6.61	5.11E-05	2.80E-05	1%	3.09E-11	1.71E-09	4.701	8.76E-10	4.51
7.61	4.99E-05	3.10E-05	1%	3.01E-11	1.67E-09	4.701	1.23E-09	4.25
8.61	5.03E-05	3.41E-05	1%	3.04E-11	1.69E-09	4.701	1.85E-09	4.65
9.61	4.83E-05	3.70E-05	1%	2.92E-11	1.62E-09	4.701	3.14E-09	5.03
10.61	4.53E-05	3.97E-05	1%	2.74E-11	1.52E-09	4.701	5.89E-09	5.42
11.61	4.50E-05	4.24E-05	1%	2.72E-11	1.51E-09	4.701	1.06E-08	5.89
12.61	4.63E-05	4.51E-05	1%	2.80E-11	1.55E-09	4.701	1.59E-08	5.09
13.61	4.38E-05	4.78E-05	1%	2.65E-11	1.47E-09	4.701	2.22E-08	4.81
14.61	4.43E-05	5.04E-05	1%	2.69E-11	1.49E-09	4.701	2.83E-08	5.47
15.61	4.43E-05	5.31E-05	1%	2.69E-11	1.49E-09	4.701	3.43E-08	4.71
16.61	4.34E-05	5.57E-05	1%	2.63E-11	1.46E-09	4.701	4.15E-08	4.59
17.61	4.34E-05	5.83E-05	1%	2.63E-11	1.46E-09	4.700	4.74E-08	4.47
18.61	4.30E-05	6.09E-05	1%	2.61E-11	1.45E-09	4.700	5.03E-08	4.22
19.61	4.33E-05	6.35E-05	1%	2.63E-11	1.46E-09	4.700	5.45E-08	4.46
20.61	4.23E-05	6.60E-05	1%	2.57E-11	1.43E-09	4.700	5.87E-08	4.56

Table 4.8 Dissolution data of Experiment 18 serpentine react in solution with H<sub>3</sub>PO<sub>4</sub>.

21.61	4.28E-05	6.86E-05	1%	2.60E-11	1.44E-09	4.700	6.36E-08	4.59
22.61	4.82E-05	7.15E-05	2%	2.93E-11	1.63E-09	4.700	6.14E-08	4.18
23.61	4.34E-05	7.41E-05	2%	2.64E-11	1.47E-09	4.700	7.13E-08	4.40
24.61	4.33E-05	7.67E-05	2%	2.64E-11	1.46E-09	4.700	8.18E-08	4.37
25.61	4.15E-05	7.92E-05	2%	2.53E-11	1.40E-09	4.700	8.99E-08	4.21
27.61	4.05E-05	8.40E-05	2%	2.47E-11	1.37E-09	4.700	1.02E-07	3.94
29.61	3.96E-05	8.88E-05	2%	2.42E-11	1.34E-09	4.700	1.17E-07	4.04
31.61	3.85E-05	9.34E-05	2%	2.35E-11	1.30E-09	4.699	1.32E-07	4.40
33.61	3.83E-05	9.80E-05	2%	2.34E-11	1.30E-09	4.699	1.65E-07	4.58
35.61	3.62E-05	1.02E-04	2%	2.22E-11	1.23E-09	4.699	1.97E-07	3.68
37.61	3.57E-05	1.07E-04	2%	2.19E-11	1.21E-09	4.698	2.25E-07	4.25
39.61	3.31E-05	1.11E-04	2%	2.03E-11	1.13E-09	4.698	2.50E-07	4.00
41.61	3.50E-05	1.15E-04	2%	2.14E-11	1.19E-09	4.698	2.76E-07	3.74
43.61	3.59E-05	1.19E-04	3%	2.20E-11	1.22E-09	4.698	2.52E-07	3.62
45.61	3.32E-05	1.23E-04	3%	2.04E-11	1.13E-09	4.698	2.45E-07	3.78
47.61	3.79E-05	1.28E-04	3%	2.33E-11	1.29E-09	4.698	2.50E-07	3.84
49.61	3.33E-05	1.32E-04	3%	2.05E-11	1.14E-09	4.698	2.62E-07	3.59
51.61	3.34E-05	1.36E-04	3%	2.06E-11	1.14E-09	4.698	2.73E-07	3.46
53.61	3.40E-05	1.40E-04	3%	2.09E-11	1.16E-09	4.698	2.90E-07	3.60
55.61	3.45E-05	1.44E-04	3%	2.13E-11	1.18E-09	4.697	3.08E-07	3.73
57.61	3.20E-05	1.48E-04	3%	1.98E-11	1.10E-09	4.697	3.41E-07	3.65
59.61	3.12E-05	1.51E-04	3%	1.92E-11	1.07E-09	4.696	4.09E-07	3.83
61.61	3.19E-05	1.55E-04	3%	1.97E-11	1.10E-09	4.696	4.54E-07	3.77
63.61	2.99E-05	1.59E-04	3%	1.85E-11	1.03E-09	4.695	4.93E-07	3.98
65.61	3.04E-05	1.63E-04	3%	1.88E-11	1.04E-09	4.696	5.33E-07	3.57
67.61	3.11E-05	1.66E-04	4%	1.93E-11	1.07E-09	4.696	4.80E-07	3.47
69.61	3.30E-05	1.70E-04	4%	2.04E-11	1.14E-09	4.696	4.53E-07	3.44
71.61	3.09E-05	1.74E-04	4%	1.92E-11	1.07E-09	4.696	4.40E-07	3.34
73.61	3.15E-05	1.78E-04	4%	1.95E-11	1.09E-09	4.696	4.33E-07	3.22

75.61	3.31E-05	1.82E-04	4%	2.06E-11	1.14E-09	4.696	4.33E-07	3.17
77.61	3.03E-05	1.85E-04	4%	1.88E-11	1.05E-09	4.696	4.53E-07	3.09
79.61	3.11E-05	1.89E-04	4%	1.93E-11	1.07E-09	4.695	4.71E-07	2.49
81.61	3.06E-05	1.93E-04	4%	1.90E-11	1.06E-09	4.694	5.18E-07	3.35
83.61	2.88E-05	1.96E-04	4%	1.79E-11	9.96E-10	4.693	6.30E-07	3.09
85.61	2.86E-05	2.00E-04	4%	1.78E-11	9.90E-10	4.693	7.08E-07	3.24
87.61	2.81E-05	2.03E-04	4%	1.76E-11	9.75E-10	4.692	7.68E-07	2.76
89.61	2.93E-05	2.06E-04	4%	1.83E-11	1.02E-09	4.693	8.14E-07	2.98
91.61	2.86E-05	2.10E-04	4%	1.78E-11	9.91E-10	4.694	7.01E-07	1.69
93.61	3.01E-05	2.14E-04	5%	1.88E-11	1.04E-09	4.695	6.37E-07	2.82
95.61	3.02E-05	2.17E-04	5%	1.89E-11	1.05E-09	4.695	5.98E-07	2.81
97.61	3.01E-05	2.21E-04	5%	1.89E-11	1.05E-09	4.695	5.72E-07	2.76
99.61	3.04E-05	2.24E-04	5%	1.91E-11	1.06E-09	4.695	5.55E-07	2.65

Time (h)	[Mg <sup>2+</sup> ] mol/l	Cumulative Mg (mol)	Fraction Reacted%	Reaction Rate (mol Mg m <sup>-2</sup> s <sup>-1</sup> )	Reaction Rate (mol Mg g <sup>-1</sup> s <sup>-1</sup> )	Effluent pH	$[\mathbf{H}^{+}] \mathbf{mol/l}$
0.11	1.30E-03	1.69E-05	0%	1.13E-08	4.35E-08	P	2.24E-07
0.61	9.02E-04	4.40E-05	1%	7.88E-09	3.03E-08	4.699	3.43E-08
1.11	8.58E-04	6.97E-05	1%	7.54E-09	2.89E-08	4.701	5.71E-08
1.61	8.56E-04	9.54E-05	2%	7.54E-09	2.90E-08	4.700	6.48E-08
2.11	8.52E-04	1.21E-04	2%	7.55E-09	2.90E-08	4.700	7.05E-08
2.61	8.37E-04	1.46E-04	3%	7.45E-09	2.86E-08	4.700	7.68E-08
3.11	8.23E-04	1.71E-04	3%	7.35E-09	2.82E-08	4.700	8.59E-08
3.61	8.02E-04	1.95E-04	4%	7.19E-09	2.76E-08	4.700	9.30E-08
4.11	7.98E-04	2.19E-04	4%	7.18E-09	2.76E-08	4.700	9.82E-08
4.61	8.19E-04	2.43E-04	5%	7.40E-09	2.84E-08	4.700	1.05E-07
5.61	7.94E-04	2.91E-04	6%	7.24E-09	2.78E-08	4.700	1.17E-07
6.61	7.86E-04	3.38E-04	6%	7.22E-09	2.77E-08	4.700	1.43E-07
7.61	7.47E-04	3.83E-04	7%	6.92E-09	2.66E-08	4.699	1.64E-07
8.61	7.27E-04	4.27E-04	8%	6.79E-09	2.61E-08	4.699	1.81E-07
9.61	7.17E-04	4.70E-04	9%	6.75E-09	2.59E-08	4.699	2.14E-07
10.61	6.81E-04	5.10E-04	10%	6.45E-09	2.48E-08	4.699	2.64E-07
11.61	6.28E-04	5.48E-04	10%	5.99E-09	2.30E-08	4.698	2.97E-07
12.61	6.06E-04	5.85E-04	11%	5.82E-09	2.23E-08	4.698	3.46E-07
13.61	6.04E-04	6.21E-04	12%	5.84E-09	2.24E-08	4.697	3.97E-07
14.61	5.64E-04	6.55E-04	12%	5.49E-09	2.11E-08	4.697	4.44E-07
15.61	5.15E-04	6.86E-04	13%	5.04E-09	1.94E-08	4.696	5.02E-07
16.61	4.93E-04	7.15E-04	14%	4.85E-09	1.86E-08	4.696	5.70E-07
17.61	4.68E-04	7.43E-04	14%	4.62E-09	1.78E-08	4.695	6.37E-07
18.61	4.39E-04	7.69E-04	15%	4.37E-09	1.68E-08	4.694	7.15E-07
						4.693	

Table 4.9 Dissolution data of Experiment 20 FPX nickel tailings in solution at 0.1 bar pCO<sub>2</sub>.

19.61	4.15E-04	7.94E-04	15%	4.14E-09	1.59E-08	4 602	7.79E-07
20.61	3.90E-04	8.18E-04	16%	3.92E-09	1.50E-08	4.095	7.70E-07
21.61	3.71E-04	8.40E-04	16%	3.74E-09	1.44E-08	4.693	8.65E-07
22.61	3.34E-04	8.60E-04	16%	3.38E-09	1.30E-08	4.092	9.31E-07
23.61	3.32E-04	8.80E-04	17%	3.37E-09	1.29E-08	4.690	1.05E-06
24.61	3.09E-04	8.99E-04	17%	3.15E-09	1.21E-08	4.090	1.20E-06
25.61	2.86E-04	9.16E-04	17%	2.92E-09	1.12E-08	4.000	1.36E-06
26.61	2.56E-04	9.31E-04	18%	2.63E-09	1.01E-08	4.080	1.52E-06
27.61	2.43E-04	9.46E-04	18%	2.50E-09	9.59E-09	4.085	1.72E-06
29.61	2.20E-04	9.72E-04	19%	2.27E-09	8.71E-09	4.085	2.15E-06
31.61	1.91E-04	9.95E-04	19%	1.98E-09	7.60E-09	4.078	2.67E-06
33.61	1.56E-04	1.01E-03	19%	1.63E-09	6.26E-09	4.673	3.43E-06
35.61	1.31E-04	1.03E-03	20%	1.37E-09	5.25E-09	4.005	4.30E-06
37.61	1.05E-04	1.04E-03	20%	1.10E-09	4.23E-09	4.656	5.30E-06
39.61	8.19E-05	1.05E-03	20%	8.59E-10	3.30E-09	4.04/	6.40E-06
41.61	7.13E-05	1.06E-03	20%	7.50E-10	2.88E-09	4.030	7.61E-06
43.61	5.60E-05	1.07E-03	20%	5.90E-10	2.26E-09	4.625	8.83E-06
45.61	5.49E-05	1.07E-03	20%	5.78E-10	2.22E-09	4.614	9.49E-06
47.61	4.57E-05	1.08E-03	21%	4.82E-10	1.85E-09	4.608	1.11E-05
49.61	3.73E-05	1.08E-03	21%	3.94E-10	1.51E-09	4.594	1.23E-05
51.61	3.12E-05	1.09E-03	21%	3.30E-10	1.27E-09	4.584	1.43E-05
53.61	2.74E-05	1.09E-03	21%	2.90E-10	1.11E-09	4.568	1.55E-05
55.61	2.52E-05	1.09E-03	21%	2.67E-10	1.03E-09	4.558	1.74E-05
57.61	2.11E-05	1.10E-03	21%	2.24E-10	8.59E-10	4.543	1.89E-05
59.61	1.82E-05	1.10E-03	21%	1.93E-10	7.41E-10	4.532	2.05E-05
61.61	1.60E-05	1.10E-03	21%	1.69E-10	6.50E-10	4.520	2.17E-05
63.61	1.38E-05	1.10E-03	21%	1.46E-10	5.61E-10	4.512	2.31E-05
						4.502	

65.61	1.29E-05	1.10E-03	21%	1.36E-10	5.24E-10	4 409	2.37E-05
67.61	1.18E-05	1.11E-03	21%	1.25E-10	4.81E-10	4.490	2.44E-05
69.61	1.14E-05	1.11E-03	21%	1.21E-10	4.66E-10	4.495	2.44E-05
71.61	1.15E-05	1.11E-03	21%	1.22E-10	4.69E-10	4.495	2.47E-05
73.61	1.10E-05	1.11E-03	21%	1.16E-10	4.47E-10	4.492	2.47E-05
75.61	1.08E-05	1.11E-03	21%	1.15E-10	4.42E-10	4.492	2.49E-05
77.61	1.03E-05	1.11E-03	21%	1.10E-10	4.21E-10	4.490	2.57E-05
79.61	9.54E-06	1.11E-03	21%	1.01E-10	3.89E-10	4.484	2.60E-05
81.61	9.04E-06	1.11E-03	21%	9.60E-11	3.69E-10	4.482	2.64E-05
83.61	8.28E-06	1.11E-03	21%	8.80E-11	3.38E-10	4.480	2.74E-05
85.61	7.70E-06	1.12E-03	21%	8.19E-11	3.14E-10	4.473	2.78E-05
87.61	7.16E-06	1.12E-03	21%	7.61E-11	2.92E-10	4.471	2.82E-05
89.61	7.03E-06	1.12E-03	21%	7.48E-11	2.87E-10	4.468	2.86E-05
91.61	6.53E-06	1.12E-03	21%	6.95E-11	2.67E-10	4.466	2.86E-05
93.61	6.80E-06	1.12E-03	21%	7.23E-11	2.78E-10	4.466	2.79E-05
95.61	7.00E-06	1.12E-03	21%	7.44E-11	2.86E-10	4.471	2.79E-05
97.61	7.29E-06	1.12E-03	21%	7.76E-11	2.98E-10	4.471	2.78E-05
99.61	7.29E-06	1.12E-03	21%	7.76E-11	2.98E-10	4.471	2.76E-05
101 (1	7.245.00	1 125 02	210/	7.015 11	2.005 10	4.472	2 905 95
101.61	7.34E-06	1.12E-03	21%	7.81E-11	3.00E-10	4.470	2.80E-05

Time (h)	[Mg <sup>2+</sup> ] mol/l	Cumulative Mg (mol)	Fraction Reacted%	Reaction Rate (mol Mg m <sup>-2</sup> s <sup>-1</sup> )	Reaction Rate (mol Mg g <sup>-1</sup> s <sup>-1</sup> )	Effluent pH	[H <sup>+</sup> ] mol/l
0.11	3.13E-04	4.07E-06	0%	1.12E-09	1.05E-08	4.684	6.49E-08
0.61	3.46E-04	1.44E-05	0%	1.26E-09	1.18E-08	4.666	2.76E-07
1.11	3.15E-04	2.39E-05	1%	1.16E-09	1.08E-08	4.657	4.47E-07
1.61	2.65E-04	3.18E-05	1%	9.84E-10	9.21E-09	4.650	6.19E-07
2.61	1.95E-04	4.35E-05	1%	7.38E-10	6.90E-09	4.637	1.01E-06
3.61	1.39E-04	5.19E-05	1%	5.30E-10	4.96E-09	4.626	1.40E-06
4.61	1.03E-04	5.80E-05	2%	3.97E-10	3.71E-09	4.618	1.78E-06
5.61	8.25E-05	6.30E-05	2%	3.20E-10	3.00E-09	4.611	2.12E-06
6.61	6.95E-05	6.72E-05	2%	2.71E-10	2.54E-09	4.606	2.39E-06
7.61	6.07E-05	7.08E-05	2%	2.38E-10	2.23E-09	4.601	2.67E-06
8.61	5.40E-05	7.40E-05	2%	2.13E-10	1.99E-09	4.596	2.95E-06
9.61	4.98E-05	7.70E-05	2%	1.97E-10	1.85E-09	4.593	3.15E-06
10.61	4.46E-05	7.97E-05	2%	1.77E-10	1.66E-09	4.589	3.42E-06
11.61	4.16E-05	8.22E-05	2%	1.66E-10	1.56E-09	4.585	3.70E-06
12.61	3.98E-05	8.46E-05	2%	1.59E-10	1.49E-09	4.588	3.51E-06
13.61	3.76E-05	8.69E-05	2%	1.51E-10	1.41E-09	4.580	4.10E-06
14.61	3.59E-05	8.90E-05	3%	1.45E-10	1.35E-09	4.578	4.29E-06
15.61	3.44E-05	9.11E-05	3%	1.39E-10	1.30E-09	4.576	4.46E-06
16.61	3.37E-05	9.31E-05	3%	1.37E-10	1.28E-09	4.573	4.66E-06
17.61	3.26E-05	9.50E-05	3%	1.33E-10	1.24E-09	4.571	4.88E-06
18.61	3.19E-05	9.70E-05	3%	1.30E-10	1.22E-09	4.568	5.08E-06
19.61	3.13E-05	9.88E-05	3%	1.28E-10	1.20E-09	4.568	5.10E-06
20.61	3.14E-05	1.01E-04	3%	1.29E-10	1.20E-09	4.570	4.97E-06
21.61	3.18E-05	1.03E-04	3%	1.31E-10	1.23E-09	4.567	5.25E-06
22.61	3.16E-05	1.05E-04	3%	1.30E-10	1.22E-09	4.565	5.43E-06
23.61	3.22E-05	1.06E-04	3%	1.33E-10	1.25E-09	4.565	5.43E-06

Table 4.10 Dissolution data of Experiment 22 GK-PK21 reacts in solution at 0.1 bar pCO<sub>2</sub>.

24.61	3.19E-05	1.08E-04	3%	1.32E-10	1.24E-09	4.564	5.51E-06
26.61	3.16E-05	1.12E-04	3%	1.32E-10	1.23E-09	4.560	5.87E-06
28.61	3.13E-05	1.16E-04	3%	1.31E-10	1.23E-09	4.557	6.13E-06
30.61	3.24E-05	1.20E-04	3%	1.37E-10	1.28E-09	4.554	6.46E-06
32.61	3.14E-05	1.24E-04	3%	1.33E-10	1.25E-09	4.551	6.79E-06
34.61	3.08E-05	1.27E-04	4%	1.31E-10	1.23E-09	4.547	7.19E-06
36.61	3.05E-05	1.31E-04	4%	1.31E-10	1.23E-09	4.544	7.55E-06
38.61	2.98E-05	1.34E-04	4%	1.29E-10	1.21E-09	4.541	7.94E-06
40.61	2.91E-05	1.38E-04	4%	1.27E-10	1.19E-09	4.538	8.28E-06
42.61	2.87E-05	1.41E-04	4%	1.25E-10	1.17E-09	4.536	8.56E-06
44.61	2.91E-05	1.45E-04	4%	1.28E-10	1.20E-09	4.539	8.20E-06
46.61	3.04E-05	1.49E-04	4%	1.34E-10	1.26E-09	4.536	8.54E-06
48.61	3.05E-05	1.52E-04	4%	1.36E-10	1.27E-09	4.534	8.82E-06
50.61	3.07E-05	1.56E-04	4%	1.37E-10	1.29E-09	4.532	9.03E-06
52.61	3.11E-05	1.60E-04	5%	1.40E-10	1.31E-09	4.529	9.35E-06
54.61	3.09E-05	1.63E-04	5%	1.40E-10	1.31E-09	4.528	9.47E-06
56.61	3.03E-05	1.67E-04	5%	1.38E-10	1.30E-09	4.527	9.74E-06
58.61	3.05E-05	1.71E-04	5%	1.40E-10	1.31E-09	4.524	1.00E-05
60.61	3.07E-05	1.74E-04	5%	1.42E-10	1.33E-09	4.519	1.08E-05
62.61	3.07E-05	1.78E-04	5%	1.43E-10	1.34E-09	4.518	1.09E-05

Time (h)	[Mg <sup>2+</sup> ] mol/l	Cumulative Mg (mol)	Fraction Reacted%	Reaction Rate (mol Mg m <sup>-2</sup> s <sup>-1</sup> )	Reaction Rate (mol Mg g <sup>-1</sup> s <sup>-1</sup> )	Effluent pH	[H <sup>+</sup> ] mol/l	Mg/Si
0.11	2.17E-03	1.43E-05	0%	1.31E-09	7.25E-08	4.692	8.18E-07	14.41
0.61	3.73E-04	2.55E-05	1%	2.25E-10	1.25E-08	4.589	1.17E-05	7.21
1.11	2.36E-04	3.26E-05	1%	1.43E-10	7.92E-09	4.520	2.06E-05	6.71
1.61	1.91E-04	3.84E-05	1%	1.16E-10	6.42E-09	4.489	2.50E-05	6.38
2.11	1.57E-04	4.31E-05	1%	9.49E-11	5.27E-09	4.467	2.85E-05	6.14
2.61	1.37E-04	4.72E-05	1%	8.27E-11	4.59E-09	4.456	3.02E-05	5.96
3.11	1.25E-04	5.09E-05	1%	7.56E-11	4.20E-09	4.449	3.13E-05	5.71
3.61	1.12E-04	5.42E-05	1%	6.77E-11	3.76E-09	4.444	3.21E-05	5.59
4.11	1.04E-04	5.74E-05	1%	6.31E-11	3.50E-09	4.445	3.19E-05	5.31
4.61	9.53E-05	6.02E-05	1%	5.79E-11	3.21E-09	4.447	3.16E-05	5.07
5.61	9.30E-05	6.58E-05	1%	5.65E-11	3.14E-09	4.439	3.30E-05	4.93
6.61	8.06E-05	7.06E-05	1%	4.90E-11	2.72E-09	4.421	3.60E-05	5.02
7.61	7.46E-05	7.51E-05	2%	4.54E-11	2.52E-09	4.421	3.60E-05	4.62
8.61	6.97E-05	7.93E-05	2%	4.25E-11	2.36E-09	4.414	3.74E-05	4.39
9.61	6.38E-05	8.31E-05	2%	3.89E-11	2.16E-09	4.397	4.04E-05	4.12
10.61	6.05E-05	8.68E-05	2%	3.69E-11	2.05E-09	4.389	4.19E-05	4.05
11.61	5.97E-05	9.03E-05	2%	3.64E-11	2.02E-09	4.381	4.34E-05	4.46
12.61	5.45E-05	9.36E-05	2%	3.33E-11	1.85E-09	4.379	4.38E-05	4.20
13.61	5.26E-05	9.68E-05	2%	3.22E-11	1.79E-09	4.381	4.34E-05	4.00
14.61	5.09E-05	9.98E-05	2%	3.11E-11	1.73E-09	4.377	4.41E-05	3.96
15.61	4.98E-05	1.03E-04	2%	3.05E-11	1.69E-09	4.376	4.43E-05	3.86
16.61	4.83E-05	1.06E-04	2%	2.96E-11	1.64E-09	4.376	4.43E-05	3.80
17.61	4.69E-05	1.09E-04	2%	2.87E-11	1.60E-09	4.373	4.49E-05	3.68
18.61	4.55E-05	1.11E-04	2%	2.79E-11	1.55E-09	4.371	4.52E-05	3.66
19.61	4.62E-05	1.14E-04	2%	2.83E-11	1.57E-09	4.384	4.27E-05	3.68
20.61	4.65E-05	1.17E-04	2%	2.85E-11	1.58E-09	4.390	4.16E-05	3.72
21.61	4.50E-05	1.20E-04	3%	2.76E-11	1.53E-09	4.393	4.11E-05	3.38

Table 4.11 Dissolution data of Experiment 26 serpentine react in solution at 1 bar pCO<sub>2</sub>.

22.61	4.53E-05	1.22E-04	3%	2.78E-11	1.55E-09	4.397	4.04E-05	3.47
23.61	4.39E-05	1.25E-04	3%	2.70E-11	1.50E-09	4.391	4.15E-05	3.33
24.61	4.51E-05	1.28E-04	3%	2.77E-11	1.54E-09	4.381	4.34E-05	3.32
25.61	4.65E-05	1.30E-04	3%	2.86E-11	1.59E-09	4.377	4.42E-05	3.44
27.61	4.48E-05	1.36E-04	3%	2.76E-11	1.53E-09	4.373	4.49E-05	3.37
29.61	4.32E-05	1.41E-04	3%	2.66E-11	1.48E-09	4.371	4.52E-05	3.17
31.61	4.54E-05	1.46E-04	3%	2.80E-11	1.56E-09	4.381	4.34E-05	3.24
33.61	4.15E-05	1.51E-04	3%	2.57E-11	1.42E-09	4.355	4.84E-05	3.51
35.61	3.84E-05	1.56E-04	3%	2.37E-11	1.32E-09	4.345	5.05E-05	2.98
37.61	3.78E-05	1.61E-04	3%	2.34E-11	1.30E-09	4.347	5.01E-05	3.06
39.61	3.57E-05	1.65E-04	3%	2.21E-11	1.23E-09	4.352	4.91E-05	2.97
41.61	3.47E-05	1.69E-04	4%	2.15E-11	1.19E-09	4.353	4.90E-05	2.96
43.61	3.62E-05	1.73E-04	4%	2.24E-11	1.25E-09	4.362	4.70E-05	3.26
45.61	3.64E-05	1.78E-04	4%	2.26E-11	1.26E-09	4.373	4.50E-05	2.99
47.61	3.61E-05	1.82E-04	4%	2.24E-11	1.24E-09	4.377	4.42E-05	2.97
49.61	3.66E-05	1.86E-04	4%	2.28E-11	1.26E-09	4.361	4.72E-05	2.89
51.61	3.51E-05	1.91E-04	4%	2.18E-11	1.21E-09	4.358	4.78E-05	2.84
53.61	3.55E-05	1.95E-04	4%	2.21E-11	1.23E-09	4.356	4.83E-05	2.81
55.61	3.68E-05	1.99E-04	4%	2.29E-11	1.27E-09	4.359	4.76E-05	3.02
57.61	3.49E-05	2.03E-04	4%	2.18E-11	1.21E-09	4.342	5.13E-05	2.84
59.61	3.38E-05	2.08E-04	4%	2.11E-11	1.17E-09	4.342	5.11E-05	2.90
61.61	3.17E-05	2.11E-04	4%	1.98E-11	1.10E-09	4.332	5.33E-05	2.65
63.61	3.17E-05	2.15E-04	5%	1.98E-11	1.10E-09	4.339	5.19E-05	2.79
65.61	3.19E-05	2.19E-04	5%	2.00E-11	1.11E-09	4.343	5.10E-05	2.89
69.61	3.17E-05	2.23E-04	5%	1.98E-11	1.10E-09	4.347	4.78E-05	2.87
71.61	3.09E-05	2.26E-04	5%	1.94E-11	1.08E-09	4.359	4.73E-05	2.73
73.61	3.15E-05	2.30E-04	5%	1.98E-11	1.10E-09	4.361	4.82E-05	2.72
75.61	3.16E-05	2.34E-04	5%	1.98E-11	1.10E-09	4.356	4.84E-05	2.62

Time (h)	[Mg <sup>2+</sup> ] mol/l	Cumulative Mg (mol)	Fraction Reacted%	Reaction Rate (mol Mg m <sup>-2</sup> s <sup>-1</sup> )	Reaction Rate (mol Mg g <sup>-1</sup> s <sup>-1</sup> )	Effluent pH	[H <sup>+</sup> ] mol/l	Mg/Si
0.11	4.60E-04	3.04E-06	0.1%	2.76E-10	1.53E-08	4.701	4.01E-10	13.09
0.61	7.44E-05	5.27E-06	0.1%	4.47E-11	2.48E-09	4.701	3.53E-10	3.56
1.11	4.95E-05	6.76E-06	0.1%	2.98E-11	1.65E-09	4.701	2.88E-10	3.11
1.61	4.26E-05	8.03E-06	0.2%	2.56E-11	1.42E-09	4.701	2.86E-10	2.86
2.11	3.85E-05	9.19E-06	0.2%	2.31E-11	1.28E-09	4.701	3.18E-10	2.76
3.11	3.10E-05	1.10E-05	0.2%	1.86E-11	1.03E-09	4.701	3.45E-10	2.75
4.11	2.67E-05	1.26E-05	0.3%	1.60E-11	8.91E-10	4.701	3.94E-10	2.63
5.11	2.34E-05	1.41E-05	0.3%	1.41E-11	7.83E-10	4.701	4.45E-10	2.62
6.11	2.18E-05	1.54E-05	0.3%	1.31E-11	7.28E-10	4.701	4.93E-10	2.46
7.11	2.00E-05	1.66E-05	0.4%	1.20E-11	6.68E-10	4.701	5.48E-10	2.61
8.11	1.84E-05	1.77E-05	0.4%	1.11E-11	6.17E-10	4.701	5.95E-10	2.38
9.11	1.71E-05	1.87E-05	0.4%	1.03E-11	5.72E-10	4.701	6.53E-10	2.48
10.11	1.66E-05	1.97E-05	0.4%	1.00E-11	5.56E-10	4.701	6.99E-10	2.59
11.11	1.58E-05	2.06E-05	0.4%	9.52E-12	5.29E-10	4.701	7.50E-10	2.84
12.11	1.55E-05	2.16E-05	0.5%	9.31E-12	5.17E-10	4.701	8.07E-10	2.30
13.11	1.42E-05	2.24E-05	0.5%	8.53E-12	4.74E-10	4.701	8.67E-10	2.60
14.11	1.41E-05	2.33E-05	0.5%	8.50E-12	4.72E-10	4.701	9.26E-10	2.28
15.11	1.34E-05	2.41E-05	0.5%	8.06E-12	4.48E-10	4.701	9.93E-10	2.46
16.11	1.26E-05	2.48E-05	0.5%	7.62E-12	4.23E-10	4.701	1.06E-09	2.48
17.11	1.29E-05	2.56E-05	0.5%	7.77E-12	4.31E-10	4.701	1.14E-09	2.30
18.11	1.37E-05	2.64E-05	0.6%	8.23E-12	4.57E-10	4.701	1.23E-09	2.29
19.11	1.26E-05	2.72E-05	0.6%	7.60E-12	4.22E-10	4.701	1.31E-09	2.40
20.11	1.32E-05	2.80E-05	0.6%	7.98E-12	4.43E-10	4.701	1.40E-09	2.49
21.11	1.28E-05	2.87E-05	0.6%	7.70E-12	4.28E-10	4.701	1.49E-09	2.31
22.11	1.21E-05	2.95E-05	0.6%	7.33E-12	4.07E-10	4.701	1.61E-09	2.42
23.11	1.24E-05	3.02E-05	0.6%	7.50E-12	4.17E-10	4.701	1.73E-09	2.51
24.11	1.31E-05	3.10E-05	0.7%	7.93E-12	4.40E-10	4.701	1.82E-09	2.56

Table 4.12 Dissolution data of Experiment 27 serpentine react in solution at 0.0004 bar pCO<sub>2</sub>.
25.11	1.28E-05	3.18E-05	0.7%	7.74E-12	4.30E-10	4.701	1.95E-09	2.38
26.11	1.25E-05	3.25E-05	0.7%	7.55E-12	4.19E-10	4.701	2.07E-09	1.99
27.11	1.22E-05	3.32E-05	0.7%	7.36E-12	4.09E-10	4.701	2.20E-09	2.41
28.11	1.19E-05	3.40E-05	0.7%	7.19E-12	3.99E-10	4.701	2.32E-09	2.45
30.11	1.11E-05	3.53E-05	0.7%	6.69E-12	3.71E-10	4.701	2.54E-09	2.20
32.11	1.05E-05	3.65E-05	0.8%	6.36E-12	3.53E-10	4.701	2.78E-09	2.09
34.11	1.03E-05	3.78E-05	0.8%	6.22E-12	3.46E-10	4.701	3.04E-09	2.80
36.11	9.60E-06	3.89E-05	0.8%	5.81E-12	3.22E-10	4.701	3.35E-09	2.60
38.11	9.95E-06	4.01E-05	0.8%	6.01E-12	3.34E-10	4.701	3.75E-09	2.40
40.11	9.53E-06	4.13E-05	0.9%	5.77E-12	3.20E-10	4.701	4.23E-09	2.05
42.11	9.80E-06	4.24E-05	0.9%	5.93E-12	3.29E-10	4.701	4.79E-09	2.33
44.11	9.46E-06	4.36E-05	0.9%	5.72E-12	3.18E-10	4.701	5.39E-09	2.15
46.11	9.86E-06	4.48E-05	0.9%	5.97E-12	3.31E-10	4.701	6.23E-09	2.60
48.11	1.05E-05	4.60E-05	1.0%	6.37E-12	3.54E-10	4.701	7.02E-09	2.16
50.11	1.02E-05	4.72E-05	1.0%	6.17E-12	3.43E-10	4.701	7.81E-09	2.12
52.11	9.95E-06	4.84E-05	1.0%	6.03E-12	3.35E-10	4.701	8.45E-09	2.24
54.11	9.72E-06	4.96E-05	1.1%	5.89E-12	3.27E-10	4.701	9.09E-09	2.02
56.11	9.10E-06	5.07E-05	1.1%	5.52E-12	3.06E-10	4.701	9.34E-09	2.23
58.11	9.17E-06	5.18E-05	1.1%	5.56E-12	3.09E-10	4.701	9.84E-09	2.08
60.11	8.36E-06	5.28E-05	1.1%	5.07E-12	2.81E-10	4.701	1.07E-08	2.26
62.11	8.22E-06	5.38E-05	1.1%	4.99E-12	2.77E-10	4.701	1.18E-08	2.08
64.11	8.18E-06	5.48E-05	1.2%	4.96E-12	2.75E-10	4.701	1.33E-08	2.08
66.11	8.28E-06	5.58E-05	1.2%	5.02E-12	2.79E-10	4.701	1.54E-08	2.26
68.11	7.58E-06	5.67E-05	1.2%	4.60E-12	2.55E-10	4.701	1.75E-08	1.81
70.11	7.73E-06	5.76E-05	1.2%	4.69E-12	2.60E-10	4.701	2.11E-08	2.11
72.11	7.79E-06	5.85E-05	1.2%	4.73E-12	2.62E-10	4.701	2.49E-08	2.41
74.11	8.09E-06	5.95E-05	1.3%	4.91E-12	2.73E-10	4.701	2.92E-08	2.03
77.11	7.56E-06	6.09E-05	1.3%	4.59E-12	2.55E-10	4.701	3.37E-08	2.12
80.11	7.17E-06	6.22E-05	1.3%	4.35E-12	2.42E-10	4.701	3.52E-08	1.71
83.11	6.74E-06	6.34E-05	1.3%	4.09E-12	2.27E-10	4.701	3.91E-08	2.18
86.11	6.64E-06	6.46E-05	1.4%	4.03E-12	2.24E-10	4.701	4.66E-08	1.99

89.11	6.57E-06	6.58E-05	1.4%	3.99E-12	2.22E-10	4.700	5.57E-08	2.22
92.11	6.79E-06	6.70E-05	1.4%	4.13E-12	2.29E-10	4.700	6.68E-08	1.91
95.11	6.91E-06	6.82E-05	1.4%	4.20E-12	2.33E-10	4.700	8.21E-08	2.61
98.11	7.10E-06	6.95E-05	1.5%	4.32E-12	2.40E-10	4.700	9.19E-08	2.09
101.11	7.01E-06	7.08E-05	1.5%	4.26E-12	2.37E-10	4.700	9.49E-08	1.83
104.11	6.77E-06	7.20E-05	1.5%	4.12E-12	2.29E-10	4.700	9.71E-08	2.37
107.11	6.41E-06	7.31E-05	1.5%	3.90E-12	2.17E-10	4.700	1.02E-07	2.04
110.11	6.24E-06	7.43E-05	1.6%	3.80E-12	2.11E-10	4.700	1.10E-07	2.02
113.11	6.16E-06	7.54E-05	1.6%	3.75E-12	2.08E-10	4.700	1.20E-07	2.20
116.11	6.41E-06	7.65E-05	1.6%	3.90E-12	2.17E-10	4.700	1.24E-07	1.73
119.11	6.40E-06	7.77E-05	1.6%	3.90E-12	2.16E-10	4.700	1.25E-07	2.50
122.11	6.50E-06	7.88E-05	1.7%	3.96E-12	2.20E-10	4.700	1.25E-07	1.85

Time (h)	[Mg <sup>2+</sup> ] mol/l	Cumulative Mg (mol)	Fraction Reacted%	Reaction Rate (mol Mg m <sup>-2</sup> s <sup>-1</sup> )	Reaction Rate (mol Mg g <sup>-1</sup> s <sup>-1</sup> )
1.94	3.89E-05	7.56E-06	0.1%	2.14E-09	1.55E-08
3.78	2.95E-05	1.10E-05	0.2%	1.92E-09	1.37E-09
5.61	2.65E-05	1.41E-05	0.2%	1.78E-09	1.04E-09
7.44	2.45E-05	1.69E-05	0.2%	1.68E-09	9.36E-10
10.19	2.31E-05	2.09E-05	0.3%	1.52E-09	8.65E-10
13.86	2.10E-05	2.56E-05	0.4%	1.41E-09	8.00E-10
17.53	1.94E-05	3.00E-05	0.4%	1.46E-09	7.20E-10
22.11	2.00E-05	3.57E-05	0.5%	1.42E-09	6.66E-10
25.78	1.95E-05	4.01E-05	0.6%	1.28E-09	6.82E-10
29.44	1.76E-05	4.41E-05	0.6%	1.23E-09	6.70E-10
32.19	1.69E-05	4.70E-05	0.7%	1.24E-09	6.04E-10
35.86	1.71E-05	5.08E-05	0.7%	1.18E-09	5.86E-10
39.53	1.62E-05	5.45E-05	0.8%	1.08E-09	5.85E-10
43.19	1.48E-05	5.79E-05	0.8%	1.20E-09	5.56E-10
46.86	1.65E-05	6.16E-05	0.9%	1.19E-09	5.08E-10
50.53	1.63E-05	6.53E-05	0.9%	1.15E-09	5.65E-10
54.19	1.57E-05	6.89E-05	1.0%	1.11E-09	5.61E-10
57.86	1.52E-05	7.23E-05	1.0%	1.07E-09	5.37E-10
61.53	1.47E-05	7.56E-05	1.1%	1.06E-09	5.21E-10

Table 4.13 Dissolution data of Olivine (forsterite) react in solution at 0.1 bar pCO<sub>2</sub>. [Adapted from Caroll et al., in prep]

Time (h)	[Mg <sup>2+</sup> ] mol/l	Cumulative Mg (mol)	Fraction Reacted%	Reaction Rate (mol Mg m <sup>-2</sup> s <sup>-1</sup> )	Reaction Rate (mol Mg g <sup>-1</sup> s <sup>-1</sup> )	Effluent pH
0.11	1.46E-03	1.90E-05	4%	1.80E-09	9.76E-08	4.701
0.36	1.09E-03	3.55E-05	7%	1.40E-09	3.65E-08	4.700
0.61	9.16E-04	4.92E-05	10%	1.21E-09	3.05E-08	4.700
0.86	1.05E-03	6.50E-05	13%	1.44E-09	3.51E-08	4.699
1.11	8.49E-04	7.77E-05	16%	1.20E-09	2.83E-08	4.699
1.36	1.06E-03	9.37E-05	19%	1.56E-09	3.55E-08	4.699
1.61	8.40E-04	1.06E-04	22%	1.27E-09	2.80E-08	4.699
1.86	1.00E-03	1.21E-04	25%	1.58E-09	3.34E-08	4.698
2.11	1.05E-03	1.37E-04	28%	1.73E-09	3.48E-08	4.698
2.49	9.63E-04	1.59E-04	33%	1.70E-09	3.21E-08	4.698
2.99	8.18E-04	1.84E-04	38%	1.56E-09	2.73E-08	4.698
3.49	9.58E-04	2.12E-04	44%	2.02E-09	3.19E-08	4.698
3.99	7.59E-04	2.35E-04	49%	1.75E-09	2.53E-08	4.697
4.59	8.00E-04	2.64E-04	55%	2.09E-09	2.67E-08	4.696
5.59	5.47E-04	2.97E-04	61%	1.68E-09	1.82E-08	4.694
7.59	3.22E-04	3.35E-04	69%	1.24E-09	1.07E-08	4.680
9.59	1.40E-04	3.52E-04	73%	6.13E-10	4.68E-09	4.644
11.59	5.28E-05	3.59E-04	74%	2.43E-10	1.76E-09	4.564
15.59	1.72E-06	3.59E-04	74%	7.91E-12	1.76E-09	4.375

Table 4.14 Dissolution data of hydrotalcite react in solution at 0.1 bar pCO<sub>2</sub>. [Data collected by Connor Turvey]





Figure 4.10 Experiment 19 brucite react in solution at 0.1 bar pCO<sub>2</sub>; A) Manual measured pH compare with inline pH electrode measured pH plotted against time; B) Evolution of [Mg<sup>2+</sup>] through the duration of the flow-through dissolution experiment.



Figure 4.11 Experiment 12 brucite react in solution with HCl A) Manual measured pH compare with inline pH electrode measured pH plotted against time; B) Evolution of [Mg<sup>2+</sup>] through the duration of the flow-through dissolution experiment.



Figure 4.12 Experiment 8 brucite react in solution with HNO<sub>3</sub> A) Manual measured pH compare with inline pH electrode measured pH plotted against time; B) Evolution of [Mg<sup>2+</sup>] through the duration of the flow-through dissolution experiment.



Figure 4.13 Experiment 16 brucite react in solution with H<sub>3</sub>PO<sub>4</sub> A) Manual measured pH compare with inline pH electrode measured pH plotted against time; B) Evolution of [Mg<sup>2+</sup>] through the duration of the flowthrough dissolution experiment.



Figure 4.14 Experiment 10 Serpentine react in solution at 0.1 bar pCO<sub>2</sub>; A) Manual measured pH compare with inline pH electrode measured pH plotted against time; B) Evolution of [Mg<sup>2+</sup>] through the duration of the flow-through dissolution experiment.



Figure 4.15 Experiment 14 Serpentine react in solution with HClA) Manual measured pH compare with inline pH electrode measured pH plotted against time; B) Evolution of [Mg<sup>2+</sup>] through the duration of the flow-through dissolution experiment.



Figure 4.16 Experiment 13 Serpentine react in solution with HNO<sub>3</sub> A) Manual measured pH compare with inline pH electrode measured pH plotted against time; B) Evolution of [Mg<sup>2+</sup>] through the duration of the flow-through dissolution experiment.



Figure 4.17 Experiment 18 Serpentine react in solution with H<sub>3</sub>PO<sub>4</sub> A) Manual measured pH compare with inline pH electrode measured pH plotted against time; B) Evolution of [Mg<sup>2+</sup>] through the duration of the flow-through dissolution experiment.



Figure 4.18 Experiment 20 FPX Nickel Tailing react in solution at 0.1 bar pCO<sub>2</sub>; A) Manual measured pH compare with inline pH electrode measured pH plotted against time; B) Evolution of [Mg<sup>2+</sup>] through the duration of the flow-through dissolution experiment.



Figure 4.19 Experiment 22 Gahcho Kué Kimberlite Tailing react in solution at 0.1 bar pCO<sub>2</sub>; A) Manual measured pH compare with inline pH electrode measured pH plotted against time; B) Evolution of [Mg<sup>2+</sup>] through the duration of the flow-through dissolution experiment.



Figure 4.20 Experiment 26 Serpentine react in solution at 1 bar pCO<sub>2</sub>; A) Manual measured pH compare with inline pH electrode measured pH plotted against time; B) Evolution of [Mg<sup>2+</sup>] through the duration of the flow-through dissolution experiment.



Figure 4.21 Experiment 27 Serpentine react in solution at 0.0004 bar pCO<sub>2</sub>; A) Manual measured pH compare with inline pH electrode measured pH plotted against time; B) Evolution of [Mg<sup>2+</sup>] through the duration of the flow-through dissolution experiment.

## **B.2.4** Mass Balance Results

Experiment No.	Acid Type	Sample(s)	Mg wt% leached based on solution	Mg wt% leached based on sample mass loss	
19	Carbonic Acid H <sub>2</sub> CO <sub>3</sub>	Brucite	102.00	106.00	
12	Hydrochloric Acid HCl	Brcutie	40.00	50.00	
8	Nitric Acid HNO <sub>3</sub>	Brcutie	35.00	29.00	
16	Phosphoric Acid H <sub>3</sub> PO <sub>4</sub>	Brcutie	35.00	38.00	
10	Carbonic Acid H <sub>2</sub> CO <sub>3</sub>	Serpentine	4.50	3.50	
13	Hydrochloric Acid HCl	Serpentine	3.00	4.40	
14	Nitric Acid HNO <sub>3</sub>	Serpentine	2.30	3.47	
18	Phosphoric Acid H <sub>3</sub> PO <sub>4</sub>	Serpentine	5.00	4.40	
20	Carbonic Acid H <sub>2</sub> CO <sub>3</sub>	FPX Nickel Tailing	21.00	20.30	
22	Carbonic Acid H <sub>2</sub> CO <sub>3</sub>	Gahcho Kué Kimberlite Tailing	5.00	4.70	
26	Carbonic Acid H <sub>2</sub> CO <sub>3</sub>	Serpentine	5.00	6.40	
27	Carbonic Acid H <sub>2</sub> CO <sub>3</sub>	Serpentine	2.00	1.70	

Table 4.15 Total Mg wt% leached based on solution measurement compare to Mg wt% leached based on sample mass loss before and after the flow-through dissolution experiment.

# **B.2.5** Charge Balance Results



Figure 4.22 PHREEQC modelled [Mg<sup>2+</sup>] mol L<sup>-1</sup> versus [H<sup>+</sup>] mol L<sup>-1</sup> compared with data from brucite dissolution using the time-resolved flow-through analyzer.



Figure 4.23 PHREEQC modelled [Mg<sup>2+</sup>] mol L<sup>-1</sup> versus [H<sup>+</sup>] mol L<sup>-1</sup> compared with data from serpentine dissolution using the time-resolved flow-through analyzer.



Figure 4.24 PHREEQC modelled [Mg<sup>2+</sup>] mol L<sup>-1</sup> versus [H<sup>+</sup>] mol L<sup>-1</sup> compared with data from serpentine dissolution using the time-resolved flow-through analyzer.

#### **B.2.6** Estimation of the fraction of Mg atoms at the serpentine surface

An estimate of the fraction of Mg atoms at the surface of serpentine grains was performed based on the similar method adopted by Daval et al. (2013), who established several unit cell dimension calculation models to understand serpentine, lizardite dissolution, and Turvey 2018, who estimated the fraction of surface Mg on pyroaurite mineral surface. The number of "surface" Mg atoms corresponds to the sum of the total amount of Mg atoms in the outermost (001) face (brucite-like sheets) and the four lateral faces of the crystallite (i.e., (100), ( $\overline{1}00$ ), ( $0\overline{1}0$ 



Figure 4.25 Schematic representation of the structure of lizardite-1T. a) structure seen in the direction [010]. b) structure seen in the direction [001] (Mellini, 1982). The tetrahedra are shown in purple, the octahedra in yellow, the Si atoms in blue, the O atoms in red, the H atoms in pink, and the Mg atoms in yellow. The parameters of the mesh (dotted frame) are as follows: a = b = 5.3 Å and c = 7.2 Å (Figure after Auzende, 2003).

Table 4.16	5 Surface	Mg	fraction	calculations
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	(001)	(100), (010),(100) and (010)
	(001) surface	surfaces
Surface Mg per area (see Figure )	3	$4 \times \frac{1}{2} = 2$
Area (Å)	16.96	153.28
Surface atom density (atoms m <sup>-2</sup> )	1.78E+19	1.30E+18
BET Specific Surface Area (m g <sup>-1</sup> )		18.51
Sample size (g)		0.5
mol Mg at the lizardite surface (mol Mg)	2.74E-04	2.00E-05
Total mol Mg at the surface (mol Mg)		2.94E-04
Total mol Mg in 0.5g of lizardite		4.72E-03
The fraction of Mg at the surface (%)	6%	0.42%
The total fraction of Mg atoms at the surface (%)		6.42%

### Table 4.17 Surface Si fraction calculation

	(001) surface
Surface Si per area (see Figure )	2
Area (Å)	16.96
Surface atom density (atoms m <sup>-2</sup> )	1.18E+19
BET Specific Surface Area (m g <sup>-1</sup> )	18.51
Sample size (g)	0.5
mol Si at the lizardite surface (mol Si)	1.82E-04
Total mol Si at the surface (mol Si)	1.82E-04
Total mol Si in 0.5g of lizardite	3.25E-03
Total Fraction of Si at the surface (%)	5.6%

Appendix C Supplementary material for chapter 3



# C.1 Experimental set-up illustration

Figure 4.26 Figure illustration of disk carbonation experimental apparatus, white, green and grey disks represents solid samples moulded into dime-size disks.



Figure 4.27 Figure illustration of batch dissolution experimental setup; Shake agitation is applied through a VWR® Standard Orbital Shaker, Model 3500; Stir agitation is applied through placing a stir bar on VWR® Standard Magnetic Stirrers, 120V.



Figure 4.28 Plot of [Mg<sup>2+</sup>] mol L<sup>-1</sup> versus [H<sup>+</sup>] mol L<sup>-1</sup> from charge balance model results using PHREEQC and the experimental results from the brucite batch dissolution in solution at 0.1 bar pCO<sub>2</sub>. Charge balance models at 0.1 bar pCO<sub>2</sub> are indicated as dashed lines (see legend).



Figure 4.29 Plot of [Mg<sup>2+</sup>] mol L<sup>-1</sup> versus [H<sup>+</sup>] mol L<sup>-1</sup> from charge balance model results using PHREEQC and the experimental results from the brucite batch dissolution in H<sub>3</sub>PO<sub>4</sub>. Charge balance models in H<sub>3</sub>PO<sub>4</sub> solution at various pCO<sub>2</sub> are indicated as coloured dashed lines (see legend).



Figure 4.30 Plot of [Mg<sup>2+</sup>] mol L<sup>-1</sup> versus [H<sup>+</sup>] mol L<sup>-1</sup> from charge balance model results using PHREEQC and the experimental results from the serpentine batch dissolution in HCl (A) and HNO<sub>3</sub> (B). Charge balance models at various pCO<sub>2</sub> are indicated with coloured dashed lines (see legend).



Figure 4.31 Plot of [Mg<sup>2+</sup>] mol L<sup>-1</sup> versus [H<sup>+</sup>] mol L<sup>-1</sup> from charge balance model results using PHREEQC and the experimental results from the serpentine batch dissolution in solution at 0.1 bar pCO<sub>2</sub>. Charge balance models at 0.1 bar pCO<sub>2</sub> are indicated as the dashed line.



Figure 4.32 Plot of [Mg<sup>2+</sup>] mol L<sup>-1</sup> versus [H<sup>+</sup>] mol L<sup>-1</sup> from charge balance model results using PHREEQC and the experimental results from the serpentine batch dissolution in HCl (A) and HNO<sub>3</sub> (B). Charge balance models at various pCO<sub>2</sub> are indicated with coloured dashed lines (see legend).



Figure 4.33 Plot of [Mg<sup>2+</sup>] mol L<sup>-1</sup> versus [H<sup>+</sup>] mol L<sup>-1</sup> from charge balance model results using PHREEQC and the experimental results from the serpentine batch dissolution in H<sub>3</sub>PO<sub>4</sub>. Charge balance models in H<sub>3</sub>PO<sub>4</sub> solution at various pCO<sub>2</sub> are indicated as coloured dashed lines (see legend).

### C.3 X-ray diffraction results

All minerals and tailings samples were identified using X-ray powder diffraction methods (XRD). Aliquots were ground under ethanol for three minutes using a McCrone® micronizing mill and agate grinding elements. Micronized aliquots were dried for ~24 h and gently disaggregated with an agate mortar and pestle. Powder mounts were prepared against the ground glass to minimize preferred orientation (Raudsepp and Pani, 2003). Quantitative phase analysis using Rietveld refinement was performed on aliquots of the brucite, quartz, serpentine and tailings samples. Ten replicates of the serpentine sample were analyzed to ensure homogenous sampling. Three replicates of the brucite and quartz mix sample, tailings samples were analyzed, and average values of mineral abundance measurements are reported in Appendix B.2. Representative XRD results of post-experimental solid from serpentine batch dissolution in HNO<sub>3</sub> and HCl are shown in Figure 4.34 and Figure 4.35. XRD results of solids post-dissolution are qualitative because the amount of solid after dissolution is not enough for performing quantitative XRD analysis.

All XRD data were collected using a Bruker D8 Focus Bragg-Brentano diffractometer with CoKα radiation and a step size of 0.03° over a range of 3-80°2θ at 7s/step. Fe monochromator foil, 0.6 mm divergence slit, incident and diffracted beam soller slits, and a Lynx Eye detector were used. A long fine focus Co X-ray tube was operated at 35 kV and 40 mA using a take-off angle of 6°. A rotation speed of 15 rpm was utilized for the collection of qualitative data. Search-match software by Bruker (DIFFRACplus EVA 14; Bruker AXS, 2008) was used for phase identification with reference to the International Centre for Diffraction Database PDF-4+ 2010. Rietveld refinement for quantitative phase analysis was completed using Topaz Version 3 (Bruker AXS, 2004) refinement software.



Figure 4.34 X-ray diffraction pattern of reacted solids from serpentine batch dissolution in HCl solution. Colours distinguish experiments using various agitations; The brown line represents the observed vermiculite peak locates at 7° 20 position.



Figure 4.35 X-ray diffraction pattern of reacted solids from serpentine batch dissolution in the HNO<sub>3</sub> solution. Colours distinguish experiments using various agitations; The brown line represents the observed vermiculite peak locates at 7° 2θ position.

## C.4 Batch dissolution results of serpentine

Table 4.18 Measured time series fluid chemistry and PHREEQC solution speciation calculation from serpentine batch dissolution experiments.

Experime nt Name	Time (h)	рН	Mg mol/l	Si mol/l	Al mol/l	Fe mol/l	Ca mol/l	K mol/l	si_Chrys otile	si_Lizar dite	si_Sapon ite-Mg- Mg	si_Sepiol ite	si_CO <sub>2</sub> (g)
	0.22	4.99	3.94E-04	8.57E-05	1.85E-06	2.35E-05	2.50E-06	1.28E-06	-19.65	-19.18	-19.19	-28.52	-0.25
НаСОа	0.75	5.08	3.94E-04	8.07E-05	1.85E-06	2.27E-05	2.50E-06	1.28E-06	-19.16	-18.69	-18.63	-27.95	-0.34
	1.47	5.10	3.44E-04	7.30E-05	1.85E-06	1.86E-05	2.50E-06	1.28E-06	-19.29	-18.82	-18.89	-28.27	-0.42
	2.72	5.28	3.21E-04	6.54E-05	1.85E-06	1.49E-05	6.10E-06	2.55E-05	-18.40	-17.93	-17.91	-27.24	-0.57
	4.75	5.36	3.17E-04	6.43E-05	1.85E-06	1.33E-05	8.36E-06	2.55E-05	-17.95	-17.49	-17.42	-26.67	-0.64
Serpentine	6.75	5.48	2.82E-04	5.83E-05	1.85E-06	9.84E-06	1.05E-05	2.55E-05	-17.46	-16.99	-16.92	-26.15	-0.80
Still	8.72	5.53	2.81E-04	5.62E-05	1.85E-06	8.77E-06	1.15E-05	2.55E-05	-17.20	-16.73	-16.75	-25.86	-0.83
	10.72	5.60	2.93E-04	6.16E-05	1.85E-06	8.38E-06	1.30E-05	2.55E-05	-16.65	-16.18	-15.99	-24.99	-0.88
	24.33	5.89	2.75E-04	6.22E-05	1.85E-06	3.88E-06	1.71E-05	2.55E-05	-14.98	-14.51	-14.17	-22.75	-1.18
	25.98	5.95	2.84E-04	6.48E-05	1.85E-06	3.51E-06	1.82E-05	2.55E-05	-14.55	-14.08	-13.75	-22.12	-1.20
	71.95	6.40	3.15E-04	9.04E-05	1.85E-06	1.33E-07	2.00E-05	2.55E-05	-11.43	-10.96	-13.75	-17.48	-1.64

Experiments are separated based on acid types and agitation effects.

Experime nt Name	Time(h)	рН	Mg mol/l	Si mol/l	Al mol/l	Fe mol/l	Ca mol/l	K mol/l	si_Chrys otile	si_Lizar dite	si_Sapon ite-Mg- Mg	si_Sepiol ite	si_CO <sub>2</sub> (g)
	0.23	5.00	7.22E-04	1.75E-04	1.85E-06	4.23E-05	2.50E-06	1.28E-06	-18.25	-17.78	-17.18	-25.62	-0.01
	0.77	5.18	8.18E-04	1.65E-04	1.85E-06	4.68E-05	5.30E-06	1.28E-06	-17.08	-16.61	-15.81	-24.15	-0.13
	1.52	5.34	9.28E-04	1.88E-04	1.85E-06	5.39E-05	7.48E-06	1.28E-06	-15.86	-15.39	-14.30	-22.32	-0.24
	2.73	5.46	8.20E-04	1.63E-04	1.85E-06	4.52E-05	7.48E-06	1.28E-06	-15.41	-14.94	-13.86	-21.94	-0.41
H <sub>2</sub> CO <sub>3</sub>	4.77	5.62	7.61E-04	1.52E-04	1.85E-06	4.09E-05	8.60E-06	1.28E-06	-14.59	-14.12	-12.98	-20.93	-0.61
Serpentine	6.78	5.73	7.93E-04	1.58E-04	1.85E-06	4.17E-05	1.02E-05	2.55E-05	-13.86	-13.39	-12.11	-19.91	-0.68
Stir	8.73	5.84	7.58E-04	1.51E-04	1.85E-06	3.92E-05	1.07E-05	2.55E-05	-13.29	-12.82	-11.54	-19.20	-0.81
	10.73	5.96	8.12E-04	1.62E-04	1.85E-06	4.21E-05	1.12E-05	2.55E-05	-12.43	-11.96	-10.54	-17.95	-0.90
	24.37	6.36	4.60E-04	1.02E-04	1.85E-06	1.62E-05	1.34E-05	2.55E-05	-11.10	-10.63	-9.54	-16.85	-1.53
	26.22	6.42	4.44E-04	1.03E-04	1.85E-06	1.49E-05	1.37E-05	2.55E-05	-10.77	-10.30	-9.21	-16.43	-1.60
	72.00	6.89	3.75E-04	1.05E-04	1.85E-06	6.71E-06	1.59E-05	2.55E-05	-8.14	-7.67	-6.68	-12.87	-2.13

Experime nt Name	Time(h)	рН	Mg mol/l	Si mol/l	Al mol/l	Fe mol/l	Ca mol/l	K mol/l	si_Chrys otile	si_Lizar dite	si_Sapon ite-Mg- Mg	si_Sepiol ite	si_CO2 (g)
	0.25	4.98	7.30E-04	1.68E-04	1.85E-06	4.34E-05	2.50E-06	1.28E-06	-18.40	-17.93	-17.38	-25.87	0.02
	0.80	5.15	5.92E-04	1.32E-04	1.85E-06	3.28E-05	2.50E-06	9.12E-06	-17.83	-17.36	-16.82	-25.46	-0.24
	1.57	5.40	5.49E-04	1.24E-04	1.85E-06	2.88E-05	4.99E-06	2.55E-05	-16.48	-16.01	-15.31	-23.76	-0.49
	2.75	5.50	5.00E-04	1.12E-04	1.85E-06	2.40E-05	6.17E-06	2.55E-05	-16.07	-15.60	-14.90	-23.36	-0.65
H <sub>2</sub> CO <sub>3</sub>	4.80	5.75	5.02E-04	1.25E-04	1.85E-06	2.69E-05	1.02E-05	2.55E-05	-14.48	-14.01	-12.87	-21.06	-0.88
Serpentine	6.82	5.95	3.93E-04	8.82E-05	1.85E-06	1.54E-05	8.92E-06	2.55E-05	-13.88	-13.41	-12.63	-20.78	-1.14
Shake	8.77	6.15	3.57E-04	8.28E-05	1.85E-06	1.25E-05	1.02E-05	2.55E-05	-12.85	-12.38	-11.60	-19.50	-1.36
	10.77	6.43	3.29E-04	7.91E-05	1.85E-06	1.01E-05	1.05E-05	2.55E-05	-11.31	-10.84	-10.01	-17.51	-1.67
	24.40	6.94	2.24E-04	6.10E-05	1.85E-06	1.87E-06	1.22E-05	2.55E-05	-8.95	-8.48	-8.41	-14.74	-2.31
	26.02	6.96	2.22E-04	6.16E-05	1.85E-06	1.79E-06	1.27E-05	2.55E-05	-8.83	-8.36	-7.75	-14.57	-2.32
	72.03	7.73	2.16E-04	6.98E-05	1.85E-06	2.78E-08	1.45E-05	2.55E-05	-8.34	-7.87	-7.21	-13.74	-2.37
Experime nt Name	Time(h)	рН	Mg mol/l	Si mol/l	Al mol/l	Fe mol/l	Ca mol/l	K mol/l	si_Chrys otile	si_Lizar dite	si_Sapon ite-Mg- Mg	si_Sepiol ite	si_CO <sub>2</sub> (g)
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	0.50	7.17	3.66E-04	7.71E-05	1.85E-06	2.37E-05	2.50E-06	8.77E-06	-6.75	-6.28	-5.25	-11.47	-2.51
	1.00	7.47	3.42E-04	7.08E-05	1.85E-06	2.18E-05	2.50E-06	1.06E-05	-5.10	-4.64	-3.66	-9.40	-2.84
	2.00	7.82	2.78E-04	6.09E-05	1.85E-06	1.72E-05	2.50E-06	1.17E-05	-3.39	-2.92	-2.11	-7.34	-3.29
	3.50	8.24	2.91E-04	6.49E-05	1.85E-06	1.81E-05	2.50E-06	1.46E-05	-0.77	-0.31	0.53	-3.78	-3.69
HNO <sub>3</sub>	5.00	8.38	2.24E-04	5.35E-05	1.85E-06	1.34E-05	2.50E-06	1.40E-05	-0.43	0.04	0.69	-3.61	-3.95
Serpentine	7.00	8.48	2.23E-04	5.58E-05	1.85E-06	1.30E-05	4.81E-06	1.81E-05	0.19	0.66	1.27	-2.73	-4.05
Still	19.00	8.88	1.91E-04	4.76E-05	1.85E-06	1.00E-05	8.44E-06	1.56E-05	2.21	2.68	3.12	-0.34	-4.54
	25.00	8.82	1.80E-04	4.54E-05	1.85E-06	9.30E-06	9.79E-06	2.14E-05	1.75	2.22	2.62	-1.00	-4.49
	28.00	8.81	1.46E-04	6.54E-05	1.85E-06	2.17E-05	1.25E-05	2.10E-05	1.75	2.22	3.08	-0.48	-4.57
	43.00	8.95	1.45E-04	3.31E-05	1.85E-06	6.64E-06	1.33E-05	1.86E-05	1.96	2.43	2.55	-1.22	-4.72
	48.00	8.76	1.35E-04	3.15E-05	1.85E-06	5.94E-06	1.31E-05	1.32E-05	0.72	1.19	0.70	-2.89	-4.55

Experime nt Name	Time(h)	рН	Mg mol/l	Si mol/l	Al mol/l	Fe mol/l	Ca mol/l	K mol/l	si_Chrys otile	si_Lizar dite	si_Sapon ite-Mg- Mg	si_Sepiol ite	si_CO2 (g)
	0.50	7.84	4.82E-04	1.01E-04	1.85E-06	3.01E-05	2.50E-06	1.95E-05	-2.20	-1.73	-0.44	-5.07	-3.06
	1.00	8.25	4.97E-04	1.08E-04	1.85E-06	3.10E-05	2.50E-06	1.08E-05	0.34	0.81	2.16	-1.60	-3.47
	2.00	8.40	4.04E-04	9.97E-05	1.85E-06	2.44E-05	2.50E-06	2.55E-05	0.91	1.38	2.60	-0.97	-3.71
	3.50	8.50	4.21E-04	1.04E-04	1.85E-06	2.59E-05	2.50E-06	2.55E-05	1.59	2.06	3.31	-0.02	-3.80
HNO3	5.00	8.52	4.21E-04	1.04E-04	1.85E-06	2.63E-05	5.53E-06	2.10E-05	1.71	2.18	3.43	0.14	-3.81
Serpentine	7.00	8.66	3.33E-04	9.08E-05	1.85E-06	1.91E-05	6.03E-06	2.55E-05	2.13	2.60	3.68	0.49	-4.06
Stir	19.00	8.92	2.43E-04	7.56E-05	1.85E-06	1.32E-05	9.58E-06	2.55E-05	3.11	3.58	4.38	1.46	-4.47
	25.00	8.80	2.23E-04	7.32E-05	1.85E-06	1.17E-05	1.07E-05	2.55E-05	2.28	2.75	3.43	0.34	-4.37
	28.00	8.78	1.84E-04	5.84E-05	1.85E-06	9.39E-06	1.21E-05	2.38E-05	1.73	2.20	2.75	-0.71	-4.43
	43.00	8.90	1.58E-04	5.57E-05	1.85E-06	7.01E-06	1.40E-05	2.22E-05	2.20	2.67	3.12	-0.18	-4.63
	48.00	8.75	1.32E-04	5.27E-05	1.85E-06	5.10E-06	1.34E-05	2.55E-05	1.05	1.52	1.52	-1.76	-4.53

Experime nt Name	Time(h)	рН	Mg mol/l	Si mol/l	Al mol/l	Fe mol/l	Ca mol/l	K mol/l	si_Chrys otile	si_Lizar dite	si_Sapon ite-Mg- Mg	si_Sepiol ite	si_CO <sub>2</sub> (g)
	0.50	7.17	3.26E-04	7.50E-06	1.85E-06	2.02E-05	2.50E-06	1.69E-05	-8.91	-8.44	-9.11	-11.82	-2.55
	1.00	7.31	2.89E-04	6.60E-06	1.85E-06	1.77E-05	2.50E-06	2.41E-05	-8.33	-7.86	-8.64	-11.23	-2.74
	2.00	7.24	2.48E-04	5.63E-06	1.85E-06	1.47E-05	2.50E-06	2.55E-05	-9.08	-8.61	-9.55	-12.45	-2.73
	3.50	7.62	2.30E-04	5.48E-06	1.85E-06	1.32E-05	2.50E-06	2.55E-05	-6.92	-6.45	-7.44	-9.61	-3.14
HNO <sub>2</sub>	5.00	7.85	2.58E-04	6.04E-06	1.85E-06	1.55E-05	4.68E-06	2.55E-05	-5.32	-4.85	-5.70	-7.34	-3.31
Serpentine	7.00	7.99	1.95E-04	4.90E-06	1.85E-06	1.07E-05	5.07E-06	2.55E-05	-5.01	-4.54	-5.68	-7.24	-3.55
Shake	19.00	8.79	1.32E-04	3.66E-06	1.85E-06	5.71E-06	9.42E-06	2.55E-05	-1.01	-0.54	-2.09	-2.41	-4.50
	25.00	8.28	1.14E-04	3.32E-06	1.85E-06	4.45E-06	1.03E-05	2.55E-05	-4.29	-3.82	-5.45	-6.86	-4.00
	28.00	8.20	1.11E-04	2.94E-06	1.85E-06	3.67E-06	1.25E-05	2.55E-05	-4.91	-4.44	-6.15	-7.85	-3.91
	43.00	8.21	9.03E-05	2.55E-06	1.85E-06	1.87E-06	1.30E-05	2.55E-05	-5.23	-4.76	-6.87	-8.50	-3.96
	48.00	8.01	9.05E-05	2.66E-06	1.85E-06	1.47E-06	1.54E-05	2.55E-05	-6.39	-5.92	-7.75	-9.97	-3.73

Experime nt Name	Time(h)	рН	Mg mol/l	Si mol/l	Al mol/l	Fe mol/l	Ca mol/l	K mol/l	si_Chrys otile	si_Lizar dite	si_Sapon ite-Mg- Mg	si_Sepiol ite	si_CO <sub>2</sub> (g)
	0.50	6.29	2.08E-04	3.46E-06	1.85E-06	1.44E-05	2.50E-06	1.06E-05	-15.41	-14.95	-16.38	-21.60	-1.85
	1.17	6.95	1.74E-04	3.18E-06	1.85E-06	1.16E-05	2.50E-06	1.41E-05	-11.75	-11.28	-12.67	-16.84	-2.60
	2.17	6.89	1.24E-04	2.35E-06	1.85E-06	7.06E-06	2.50E-06	2.55E-05	-12.79	-12.32	-14.07	-18.67	-2.67
	5.17	7.85	1.16E-04	2.42E-06	1.85E-06	6.19E-06	2.50E-06	2.55E-05	-7.10	-6.63	-8.33	-11.04	-3.68
	7.00	7.46	1.47E-04	2.91E-06	1.85E-06	8.51E-06	4.97E-06	2.55E-05	-8.98	-8.51	-10.04	-13.28	-3.15
HCl	19.17	8.52	1.12E-04	2.23E-06	1.85E-06	4.93E-06	9.69E-06	2.55E-05	-3.23	-2.76	-4.57	-6.04	-4.32
Serpentine Still	22.17	8.59	1.20E-04	2.22E-06	1.85E-06	5.34E-06	1.07E-05	2.55E-05	-2.73	-2.26	-4.06	-5.40	-4.34
	25.17	8.76	1.25E-04	2.23E-06	1.85E-06	5.58E-06	1.17E-05	2.55E-05	-1.68	-1.21	-3.29	-4.02	-4.48
	28.17	8.30	1.18E-04	2.21E-06	1.85E-06	5.04E-06	1.19E-05	2.55E-05	-4.48	-4.01	-5.77	-7.71	-4.02
	31.17	8.59	1.28E-04	2.59E-06	1.85E-06	5.50E-06	1.27E-05	2.55E-05	-2.52	-2.05	-3.76	-4.90	-4.29
	44.17	8.60	1.12E-04	2.08E-06	1.85E-06	4.00E-06	1.35E-05	2.55E-05	-2.82	-2.35	-4.34	-5.61	-4.34
	72.33	8.50	8.53E-05	1.91E-06	1.85E-06	1.16E-06	1.64E-05	2.55E-05	-3.83	-3.36	-4.34	-7.07	-4.29

Experime nt Name	Time(h)	рН	Mg mol/l	Si mol/l	Al mol/l	Fe mol/l	Ca mol/l	K mol/l	si_Chrys otile	si_Lizar dite	si_Sapon ite-Mg- Mg	si_Sepiol ite	si_CO <sub>2</sub> (g)
	0.50	7.35	4.00E-04	7.73E-06	1.85E-06	2.52E-05	2.50E-06	1.12E-05	-7.56	-7.09	-7.64	-9.97	-2.65
	1.17	7.76	4.24E-04	8.21E-06	1.85E-06	2.63E-05	5.95E-06	9.85E-06	-4.98	-4.51	-5.02	-6.45	-3.04
	2.17	8.17	2.59E-04	4.71E-06	1.85E-06	1.60E-05	2.50E-06	1.97E-05	-3.61	-3.14	-4.15	-5.45	-3.66
	5.17	8.17	3.71E-04	7.20E-06	1.85E-06	2.18E-05	1.08E-05	2.55E-05	-2.81	-2.34	-2.99	-3.76	-3.50
	7.00	8.54	3.14E-04	6.34E-06	1.85E-06	1.82E-05	1.10E-05	2.55E-05	-0.93	-0.46	-1.26	-1.47	-3.94
HCl	19.17	9.03	2.11E-04	4.10E-06	1.85E-06	1.18E-05	1.11E-05	2.55E-05	1.07	1.54	0.25	0.45	-4.64
Serpentine Stir	22.17	8.96	1.88E-04	3.64E-06	1.85E-06	9.98E-06	1.16E-05	2.55E-05	0.42	0.89	-0.52	-0.57	-4.60
	25.17	8.83	2.00E-04	3.87E-06	1.85E-06	1.09E-05	1.20E-05	2.55E-05	-0.21	0.26	-1.10	-1.28	-4.42
	28.17	8.72	1.52E-04	3.57E-06	1.85E-06	6.78E-06	1.22E-05	2.55E-05	-1.26	-0.79	-2.54	-2.77	-4.40
	31.17	8.73	1.49E-04	3.32E-06	1.85E-06	6.83E-06	1.18E-05	2.55E-05	-1.29	-0.82	-2.45	-2.92	-4.41
	44.17	8.84	1.33E-04	3.41E-06	1.85E-06	4.73E-06	1.45E-05	2.55E-05	-0.77	-0.30	-2.10	-2.21	-4.53
	72.33	8.85	1.12E-04	3.72E-06	1.85E-06	1.92E-06	1.60E-05	2.55E-05	-0.85	-0.38	-2.30	-2.20	-4.60

Experime nt Name	Time(h)	рН	Mg mol/l	Si mol/l	Al mol/l	Fe mol/l	Ca mol/l	K mol/l	si_Chrys otile	si_Lizar dite	si_Sapon ite-Mg- Mg	si_Sepiol ite	si_CO <sub>2</sub> (g)
	0.50	6.66	2.00E-04	3.70E-05	1.85E-06	1.26E-05	2.50E-06	6.16E-06	-11.18	-10.71	-10.43	-18.53	-2.25
	1.17	6.97	1.87E-04	3.63E-05	1.85E-06	1.14E-05	2.50E-06	1.54E-05	-9.42	-8.95	-8.66	-16.21	-2.59
	2.17	7.33	1.73E-04	3.31E-05	1.85E-06	9.97E-06	2.50E-06	1.76E-05	-7.44	-6.97	-6.71	-13.70	-2.99
	5.17	8.06	1.88E-04	3.45E-05	1.85E-06	1.11E-05	4.88E-06	2.23E-05	-2.93	-2.46	-2.21	-7.65	-3.69
	7.00	7.91	1.97E-04	3.44E-05	1.85E-06	1.14E-05	6.27E-06	2.11E-05	-3.77	-3.31	-3.01	-8.77	-3.51
HCl	19.17	8.06	1.24E-04	2.47E-05	1.85E-06	5.23E-06	1.04E-05	2.55E-05	-3.74	-3.28	-3.60	-9.22	-3.83
Serpentine	22.17	8.01	1.12E-04	2.43E-05	1.85E-06	4.19E-06	1.14E-05	2.55E-05	-4.18	-3.72	-3.87	-9.82	-3.81
	25.17	7.91	1.02E-04	2.19E-05	1.85E-06	3.34E-06	1.14E-05	2.55E-05	-4.99	-4.52	-3.87	-11.05	-3.74
	28.17	7.76	1.02E-04	2.12E-05	1.85E-06	3.08E-06	1.22E-05	2.55E-05	-5.92	-5.45	-3.87	-12.32	-3.60
	31.17	7.71	1.01E-04	2.18E-05	1.85E-06	2.76E-06	1.32E-05	2.55E-05	-6.20	-5.74	-3.87	-12.67	-3.53
	44.17	7.90	8.41E-05	1.98E-05	1.85E-06	1.43E-06	1.39E-05	2.55E-05	-5.38	-4.91	-5.33	-11.71	-3.80
	72.33	7.80	9.81E-05	2.23E-05	1.85E-06	7.17E-07	1.77E-05	2.55E-05	-5.69	-5.22	-5.33	-11.94	-3.61

Experime nt Name	Time(h)	рН	Mg mol/l	Si mol/l	Al mol/l	Fe mol/l	Ca mol/l	K mol/l	si_Chrys otile	si_Lizar dite	si_Sapon ite-Mg- Mg	si_Sepiol ite	si_CO <sub>2</sub> (g)
	0.25	5.28	7.00E-05	2.15E-06	1.85E-06	2.69E-07	2.50E-06	2.55E-05	-23.30	-22.83	-25.45	-32.81	-0.77
	0.75	5.66	6.11E-05	1.43E-06	1.85E-06	2.69E-07	2.50E-06	2.55E-05	-21.55	-21.09	-23.73	-31.07	-1.12
	1.25	6.07	6.64E-05	1.70E-06	1.85E-06	2.69E-07	2.50E-06	2.55E-05	-18.84	-18.37	-20.63	-27.20	-1.50
	3.75	6.65	5.60E-05	1.66E-06	1.85E-06	2.69E-07	2.50E-06	2.55E-05	-15.60	-15.13	-17.20	-22.92	-2.09
H <sub>3</sub> PO <sub>4</sub>	5.25	6.66	5.70E-05	1.83E-06	1.85E-06	2.69E-07	5.22E-06	2.55E-05	-15.44	-14.97	-16.96	-22.56	-2.07
Serpentine	7.25	6.76	7.26E-05	2.32E-06	1.85E-06	2.69E-07	6.53E-06	2.55E-05	-14.33	-13.86	-15.62	-20.74	-2.12
Still	21.75	6.96	6.47E-05	2.55E-06	1.85E-06	2.69E-07	7.91E-06	2.55E-05	-13.19	-12.72	-14.60	-19.08	-2.36
	24.75	7.11	7.06E-05	2.81E-06	1.85E-06	2.69E-07	9.28E-06	2.55E-05	-12.10	-11.63	-13.30	-17.49	-2.47
	27.75	7.10	7.31E-05	2.79E-06	1.85E-06	2.69E-07	1.03E-05	2.55E-05	-12.12	-11.66	-13.26	-17.53	-2.45
	30.75	7.06	6.87E-05	2.88E-06	1.85E-06	2.69E-07	9.82E-06	2.55E-05	-12.42	-11.95	-13.96	-17.87	-2.42
	47.25	7.09	8.59E-05	3.52E-06	1.85E-06	2.69E-07	1.30E-05	2.55E-05	-11.78	-11.31	-13.12	-16.74	-2.40

Experime nt Name	Time(h)	рН	Mg mol/l	Si mol/l	Al mol/l	Fe mol/l	Ca mol/l	K mol/l	si_Chrys otile	si_Lizar dite	si_Sapon ite-Mg- Mg	si_Sepiol ite	si_CO2 (g)
	0.25	6.50	2.68E-04	4.74E-06	1.85E-06	8.49E-11	2.50E-06	1.61E-05	-13.57	-13.10	-14.14	-18.69	-1.95
	0.75	6.72	2.24E-04	4.22E-06	1.85E-06	7.56E-11	5.52E-06	2.55E-05	-12.58	-12.11	-13.25	-17.53	-2.24
	1.25	6.88	1.67E-04	3.99E-06	1.85E-06	7.15E-11	7.19E-06	2.55E-05	-12.03	-11.56	-12.73	-16.88	-2.49
	3.75	7.00	1.16E-04	2.80E-06	1.85E-06	2.69E-07	7.15E-06	2.55E-05	-12.07	-11.60	-13.17	-17.46	-2.76
H <sub>3</sub> PO <sub>4</sub>	5.25	7.03	8.89E-05	2.64E-06	1.85E-06	2.69E-07	7.05E-06	2.55E-05	-12.28	-11.82	-13.51	-17.82	-2.83
Serpentine	7.25	7.11	9.03E-05	3.05E-06	1.85E-06	2.69E-07	8.47E-06	2.55E-05	-11.67	-11.20	-12.67	-16.79	-2.79
Stir	21.75	7.28	9.48E-05	4.07E-06	1.85E-06	2.69E-07	1.17E-05	2.55E-05	-10.34	-9.87	-11.59	-14.60	-2.95
	24.75	7.19	9.68E-05	4.20E-06	1.85E-06	2.69E-07	1.21E-05	2.55E-05	-10.83	-10.36	-11.69	-15.22	-2.79
	27.75	7.10	1.03E-04	4.29E-06	1.85E-06	2.69E-07	1.26E-05	2.55E-05	-11.27	-10.81	-12.31	-15.77	-2.68
	30.75	7.15	9.10E-05	4.41E-06	1.85E-06	2.69E-07	1.17E-05	2.55E-05	-11.11	-10.64	-11.95	-15.51	-2.75
	47.25	7.18	1.08E-04	5.00E-06	1.85E-06	2.69E-07	1.45E-05	2.55E-05	-10.61	-10.14	-11.49	-14.66	-2.73

Experime nt Name	Time(h)	рН	Mg mol/l	Si mol/l	Al mol/l	Fe mol/l	Ca mol/l	K mol/l	si_Chrys otile	si_Lizar dite	si_Sapon ite-Mg- Mg	si_Sepiol ite	si_CO2 (g)
	0.25	5.83	2.55E-04	4.81E-06	1.85E-06	1.75E-05	2.50E-06	2.55E-05	-17.64	-17.17	-18.47	-24.10	-1.28
	0.75	5.92	2.03E-04	4.19E-06	1.85E-06	1.37E-05	2.50E-06	2.55E-05	-17.50	-17.03	-18.48	-24.11	-1.47
	1.25	6.34	1.87E-04	4.10E-06	1.85E-06	1.20E-05	7.35E-06	2.55E-05	-15.10	-14.63	-15.90	-20.94	-1.92
	3.75	6.64	8.42E-05	2.77E-06	1.85E-06	2.69E-06	6.06E-06	2.55E-05	-14.64	-14.17	-15.78	-20.89	-2.60
H <sub>3</sub> PO <sub>4</sub>	5.25	6.60	7.48E-05	2.81E-06	1.85E-06	2.69E-06	6.09E-06	1.46E-05	-15.01	-14.54	-16.27	-21.37	-2.66
Serpentine	7.25	6.82	7.02E-05	2.90E-06	1.85E-06	2.69E-06	7.39E-06	2.55E-05	-13.75	-13.28	-14.89	-19.64	-2.86
Shake	21.75	7.03	6.73E-05	4.35E-06	1.85E-06	2.69E-06	9.59E-06	2.55E-05	-12.19	-11.72	-13.16	-16.98	-3.08
	24.75	7.07	9.40E-05	4.90E-06	1.85E-06	2.69E-06	1.08E-05	2.55E-05	-11.43	-10.96	-12.41	-15.79	-2.93
	27.75	7.10	7.51E-05	4.91E-06	1.85E-06	2.69E-06	1.14E-05	2.55E-05	-11.54	-11.07	-12.41	-15.93	-2.99
	30.75	6.97	8.41E-05	5.06E-06	1.85E-06	2.69E-06	1.19E-05	2.55E-05	-12.15	-11.69	-12.91	-16.71	-2.72
	47.25	7.02	8.62E-05	5.57E-06	1.85E-06	2.69E-06	1.34E-05	2.55E-05	-11.74	-11.27	-12.42	-16.02	-2.75

## C.5 Batch dissolution results of brucite

Table 4.19 Measured time series fluid chemistry and PHREEQC solution speciation calculation from brucite batch dissolution experiments.

Experime nt Name	Time (h)	рН	Mg (ppm)	Brucite Saturat ion Index (Ω)	Cumul ative Mg%	Experim ent Name	Time (h)	рН	Mg (ppm)	Brucite Saturat ion Index (Ω)	Cumul ative Mg%	Experime nt Name	Time (h)	рН	Mg (ppm)	Brucite Saturat ion Index (Ω)	Cumul ative Mg%
	0.22	4.63	0.36	-12.56	1%		0.25	4.86	1.29	-12.43	4%		0.50	4.26	1.40	-11.35	4%
	0.55	4.66	0.35	-12.56	1%		0.75	5.00	1.97	-12.40	6%		1.00	4.85	2.20	-11.30	7%
	1.32	4.78	0.62	-12.25	2%		1.25	5.08	2.82	-12.07	9%		1.50	5.01	3.20	-11.69	10%
	2.63	4.88	0.96	-12.03	3%		3.25	5.27	4.78	-11.97	15%		2.50	5.21	4.33	-11.48	14%
H <sub>2</sub> CO <sub>3</sub>	4.65	5.06	1.54	-11.79	4%	H <sub>2</sub> CO <sub>3</sub>	6.25	5.51	7.09	-11.77	22%		3.50	5.33	5.54	-11.31	17%
Brucite	6.70	5.40	2.66	-11.49	7%	Brucite	19.25	5.83	13.92	-11.64	44%	H <sub>2</sub> CO <sub>3</sub> Brucite	5.50	5.48	8.54	-11.19	27%
Still	8.65	5.51	4.84	-11.23	14%	Stir	23.25	5.91	15.62	-11.52	49%	Shake	7.50	5.56	9.29	-11.00	29%
	10.67	5.62	5.50	-11.17	15%		28.25	6.00	18.88	-11.64	59%		22.75	5.95	17.92	-10.96	56%
	24.27	6.13	9.94	-10.91	28%		45.25	6.11	26.45	-11.45	83%		26.75	5.98	20.05	-10.68	63%
	25.80	6.17	10.30	-10.89	29%		48.00	6.14	25.16	-11.21	79%		31.25	6.06	22.31	-10.63	70%
	71.90	6.79	15.66	-10.72	44%		50.00	6.15	28.50	-11.22	89%		47.25	6.16	29.59	-10.59	93%
													49.25	6.09	29.73	-10.47	93%

Experiments are separated based on acid types and agitation effects.

Experi ment Name	Time (h)	рН	Mg (ppm)	Brucite Saturati on Index (Ω)	Cumu lative Mg%	Experi ment Name	Time (h)	рН	Mg (ppm)	Brucite Saturat ion Index (Ω)	Cumul ative Mg%	Experi ment Name	Time (h)	рН	Mg (ppm)	Brucite Saturat ion Index (Ω)	Cumul ative Mg%
	0.33	5.76	0.78	-8.65	2%		0.33	5.98	0.92	-11.83	0%		0.33	5.38	0.66	-11.21	0%
	0.83	7.05	0.85	-8.57	3%		0.83	6.65	1.20	-11.78	4%		0.83	6.56	0.81	-11.00	4%
	1.83	7.41	1.08	-7.39	3%		1.83	8.71	-	-10.63			1.83	7.14	1.05	-9.37	5%
	3.83	9.12	1.73	-6.29	5%		3.83	9.42	2.05	-7.20	6%		3.83	8.99	1.57	-6.42	6%
HNO3	6.83	9.19	1.85	-5.84	6%	HNO3	6.83	9.44	2.26	-6.61	7%	HNO3	6.83	9.10	1.84	-2.94	7%
Brucite	19.83	9.64	2.79	-5.43	9%	Brucite	19.83	9.72	3.14	-5.45	10%	Brucite	19.83	9.56	2.68	-1.94	10%
Still	22.83	9.59	2.88	-4.79	9%	Stir	22.83	9.67	3.30	-3.15	10%	Shake	22.83	9.49	2.78	-1.34	10%
	23.83	9.55	3.04	-3.35	10%		23.83	9.56	3.54	-2.17	11%		23.83	9.43	2.67	-1.08	11%
	27.27	9.31	3.21	-2.31	10%		27.27	9.25	3.50	-1.52	11%		27.27	9.36	3.08	-0.92	11%
	43.83	9.54	3.54	-2.39	11%		43.83	9.68	3.75	-1.33	12%		43.83	9.27	3.26	-0.89	12%
	46.57	9.68	3.58	-2.42	11%		46.57	9.64	3.84	-1.37	12%		46.57	9.35	3.50	-0.90	12%

Experi ment Name	Time (h)	рН	Mg (ppm)	Brucite Saturat ion Index (Ω)	Cumul ative Mg%	Experi ment Name	Time (h)	рН	Mg (ppm)	Brucite Saturat ion Index (Ω)	Cumul ative Mg%	Experi ment Name	Time (h)	рН	Mg (ppm)	Brucite Saturat ion Index (Ω)	Cumul ative Mg%
	0.37	4.73	0.38	-11.64	1%		0.38	4.83	0.35	-11.47	1%		0.32	4.73	0.53	-11.50	2%
	0.67	5.03	0.53	-10.90	2%		0.67	5.10	0.46	-10.82	1%		0.52	5.00	0.61	-10.90	2%
	1.08	5.62	0.53	-9.72	2%		1.13	5.74	0.57	-9.95	2%		1.08	6.17	0.76	-8.46	2%
	2.07	6.72	0.75	-7.37	2%		2.10	6.58	0.75	-7.65	2%		2.07	7.35	1.02	-5.98	3%
HC1	3.08	7.26	0.90	-6.21	3%	HC1	3.17	7.15	0.81	-6.47	3%	HCl	3.17	8.59	1.25	-3.41	4%
Brucite	5.05	8.57	1.01	-8.28	3%	Brucite	5.05	8.55	1.14	-3.53	4%	Brucite	5.10	9.15	1.57	-2.20	5%
Still	8.05	9.17	1.40	-2.21	4%	Stir	8.08	9.21	1.59	-2.07	5%	Shake	8.82	9.47	2.03	-1.45	6%
	24.03	9.59	2.11	-1.19	7%		24.05	9.60	1.91	-1.21	6%		24.33	9.66	3.06	-0.90	10%
	26.02	9.52	2.10	-1.33	7%		26.07	9.54	2.29	-1.26	7%		26.28	9.59	3.00	-1.04	9%
	28.02	9.52	2.16	-1.36	7%		28.07	9.55	2.25	-1.24	7%		28.08	9.59	3.04	-1.04	10%
	30.03	9.50	2.25	-1.35	7%		30.08	9.52	2.34	-1.29	7%		30.25	9.54	3.04	-1.14	10%

Experi ment Name	Time (h)	рН	Mg (ppm)	Brucite Saturat ion Index (Ω)	Cumul ative Mg%	Experi ment Name	Time (h)	рН	Mg (ppm)	Brucite Saturat ion Index (Ω)	Cumul ative Mg%	Experi ment Name	Time (h)	рН	Mg (ppm)	Brucite Saturat ion Index (Ω)	Cumul ative Mg%
	0.50	4.90	0.58	-11.13	2%		0.50	5.46	1.09	-9.73	3%	H <sub>3</sub> PO <sub>4</sub> Brucite	0.50	4.65	0.64	-11.58	2%
	0.75	4.98	0.75	-10.85	2%	HJPO4	0.75	5.96	1.21	-8.69	4%		0.75	4.87	0.79	-11.05	2%
	1.75	5.24	0.78	-10.32	2%		1.75	6.53	1.46	-7.47	5%		1.75	5.38	0.88	-9.98	3%
	2.75	6.30	1.14	-8.03	4%		2.75	7.08	1.89	-6.26	6%		2.75	6.26	1.21	-8.09	4%
H <sub>3</sub> PO <sub>4</sub> Brucite Still	5.75	6.91	1.56	-6.68	5%		5.75	8.28	2.73	-3.86	9%		5.75	6.95	1.73	-6.56	5%
	9.75	7.60	1.99	-5.20	6%	Brucite	9.75	9.18	2.94	-1.88	9%		9.75	7.54	2.15	-5.29	7%
	21.75	9.17	3.00	-1.89	9%	Stir	21.75	9.53	3.82	-1.07	12%	Shake	21.75	8.96	2.73	-2.34	9%
	26.75	9.24	4.33	-1.59	14%		26.75	9.57	4.14	-0.95	13%		26.75	9.04	2.92	-2.16	9%
	43.75	9.53	3.71	-1.08	12%		43.75	9.69	4.47	-0.68	14%		43.75	9.32	3.49	-1.52	11%
	51.75	9.40	3.99	-1.31	12%		51.75	9.65	4.43	-0.76	14%		51.75	9.24	3.44	-1.69	11%
	55.75	9.46	4.07	-1.18	13%		55.75	9.63	4.55	-0.79	14%		55.75	9.20	3.66	-1.75	11%

# C.6 Detailed disk carbonation results

Sample #	Time (h)	Carbon Content gained (Cf-Ci) (%)
BrQtz0	0	0.000
BrQtz1	19	0.084
BrQtz2	30	0.095
BrQtz3	44	0.146
BrQtz4	67	0.312
BrQtz5	97	0.226
BrQtz6	119	0.371
BrQtz7	144	0.426

Table 4.20 Disk carbonation results of experiment 1, 10%Br90%Quartz.

### Table 4.21 Disk carbonation results of experiment 2, 10%Br90%Quartz.

Sample #	Time (h)	Carbon Content gained (Cf-Ci) (%)
BrQtz0	0	0.000
BrQtz1	25	0.344
BrQtz2	48	0.432
BrQtz3	96	0.440
BrQtz4	145	0.428
BrQtz5	171	0.319
BrQtz6	196	0.520
BrQtz7	220	0.465
BrQtz8	258	0.558
BrQtz9	330	0.515
BrQtz10	354	0.479
BrQtz11	354	0.440

### Table 4.22 Disk carbonation results of experiment 3, 10%Br90%Quartz.

Sample #	Time (h)	Carbon Content gained (Cf-Ci) (%)
BrCor0	0	0.000
BrCor1	23	0.114
BrCor2	46	0.163
BrCor3	95	0.197
BrCor4	119	0.189
BrCor5	143	0.204

BrCor6	168	0.218
BrCor7	191	0.194
BrCor8	240	0.266
BrCor9	287	0.287
BrCor10	334	0.283

#### Table 4.23 Disk carbonation results of BD-FPCOM.

Sample #	Time (h)	Carbon Content gained (Cf-Ci) (%)
BD-FPCOM0	0	0.000
BD-FPCOM1	25	0.229
BD-FPCOM2	66	0.329
BD-FPCOM3	117	0.429
BD-FPCOM4	170	0.499
BD-FPCOM5	220	0.569
BD-FPCOM6	263	0.709
BD-FPCOM7	335	0.999
BD-FPCOM8	384	1.119
BD-FPCOM9	405	1.179
BD-FPCOM10	433	1.239
BD-FPCOM11	479	1.309
BD-FPCOM12	525	1.369

#### Table 4.24 Disk carbonation results of forsterite.

Sample #	Time (h)	Carbon Content gained (Cf-Ci) (%)
Forsterite0	0	0.000
Forserite1	25	0.000
Forserite2	66	0.000
Forserite3	117	0.000
Forserite4	170	0.000
Forserite5	220	0.001
Forserite6	263	0.001
Forserite7	335	0.002
Forserite8	384	0.001
Forserite9	405	0.001
Forserite10	433	0.002
Forserite11	479	0.001
Forserite12	525	0.003

Sample #	Time (h)	Carbon Content gained (Cf-Ci) (%)
15FBD43-0	0	0.000
15FBD43-1	25	0.010
15FBD43-2	66	0.031
15FBD43-3	117	0.039
15FBD43-4	170	0.059
15FBD43-5	220	0.073
15FBD43-6	263	0.078
15FBD43-7	335	0.124
15FBD43-8	384	0.126
15FBD43-9	405	0.138
15FBD43-10	433	0.149
15FBD43-11	479	0.196
15FBD43-12	525	0.206

Table 4.25 Disk carbonation results of BD-15FPD43.

Table 4.26 Disk carbonation results of serpentine.

Sample #	Time (h)	Carbon Content gained (Cf-Ci) (%)
Serpentine0	0	0.000
Serpentine1	25	0.002
Serpentine2	66	-0.004
Serpentine3	117	-0.032
Serpentine4	170	-0.002
Serpentine5	220	0.002
Serpentine6	263	-0.001
Serpentine7	335	0.002
Serpentine8	384	-0.001
Serpentine9	405	0.005
Serpentine10	433	-0.001
Serpentine11	479	0.003
Serpentine12	525	-0.002

Sample #	Time (h)	Carbon Content gained (Cf-Ci) (%)
GK-PK21-0	0	0.000
GK-PK21-1	25	0.206
GK-PK21-2	66	0.202
GK-PK21-3	117	0.183
GK-PK21-4	170	0.181
GK-PK21-5	220	0.169
GK-PK21-6	263	0.165
GK-PK21-7	335	0.133
GK-PK21-8	384	0.133
GK-PK21-9	405	0.118
GK-PK21-10	433	0.118
GK-PK21-11	479	0.100
GK-PK21-12	525	0.110

Table 4.27 Disk carbonation results of GK-PK21.

### Table 4.28 Disk carbonation results of experiment 5, 10%Br90%Qtz.

Sample #	Time (h)	Carbon Content gained (Cf-Ci) (%)
BrQtz0	0	0.000
BrQtz1	48	0.033
BrQtz2	72	0.025
BrQtz3	96	0.057
BrQtz4	168	0.084
BrQtz5	216	0.097
BrQtz6	240	0.105
BrQtz7	266	0.103
BrQtz8	314	0.148
BrQtz9	386	0.171
BrQtz10	482	0.165